EFFECT OF MIXING ON REACTOR PERFORMANCE FOR HOMOGENEOUS SYSTEMS -
INTRODUCTION
(CHE 512)
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1. EFFECT OF MIXING ON REACTOR PERFORMANCE FOR HOMOGENEOUS SYSTEMS - INTRODUCTION

In dealing with homogeneous reaction systems we have seen that basically all problems encountered can be classified into two broad categories:

I. Reactor design is required for a given reaction system, and "a priori" prediction of reactor performance is therefore needed.
II. Assessment of performance of existing reactors is asked for, and suggestions for improvement are solicited.

So far in dealing with these problems we have assumed two limits in mixing pattern (realizing that mixing and flow patterns affect reactor performance). For systems with continuous flow at steady state they are:

• CSTR - perfectly mixed (on molecular level) tank
• PFR - plug flow reactor (no mixing in direction of flow, piston like flow)

For a single reaction at isothermal conditions, reactor performance is measured by conversion of the limiting reactant and we know that for each of the ideal reactors it is a function of kinetics, feed concentrations and thermodynamic limitations i.e

\[ x_A = f \left( Da, \frac{C_{B_0}}{C_{A_0}}, K \right) \]  

(1)

where

- \( Da \) - Damkohler Number = \( \frac{\tau_P}{\tau_R} \)
- \( C_{B_0} \) - reactant ratio in the feed
- \( C_{A_0} \)
- \( K \) - equilibrium constant

For an n-th order irreversible reaction with constant density, a mass balance on the limiting reactant A readily yields an explicit relationship for the Damkohler number as a function of conversion, which, for each of the two ideal flow patterns, takes the following form:

\[ Da_n = \frac{x_A}{(1 - x_A)^n}; \quad (CSTR) \]  

(2a)
\[ Da_n = \frac{1}{1-n} \left[ 1 - (1 - x_A)^{1-n} \right] ; \ n \neq 1 \]  
\[ Da_1 = \ell n \left( \frac{1}{1-x_A} \right) ; \ n = 1 \]  
\[ Da_1 = kC_{A_0}^{-1} \ell \]  

For example, for a first order irreversible reaction the ideal reactors design equations become:

\[ Da_i = \frac{x_A}{1-x_A} \]  
\[ x_A = \frac{Da_i}{1+Da_i} \] \hspace{1cm} (3a)  
\[ Da_i = \ell n \left( \frac{1}{1-x_A} \right) \]  
\[ x_A = 1 - e^{-Da_i} \] \hspace{1cm} (3b)

Implicitly, in deriving the above expressions, we have assumed that the feed can be intimately premixed, down to molecular level, without reaction (i.e. the mixing time in generating a homogeneous feed is extremely short compared to characteristic reaction time and no reaction occurs during that time).

Thus, we realize that besides the characteristic reaction and process time we have to worry about characteristic mixing time (or mixing intensity which is proportional to its reciprocal) and about the scale of mixing. Then

\[ \text{Reactor Performance} = f \text{ (kinetics, flow pattern, mixing intensity and scale)} \] \hspace{1cm} (4)

We can intuitively recognize that the reaction system and its performance are characterized by four parameters (in a simplistic approach):

\[ \tau_p = \frac{V}{Q} \] - characteristic process time
\[ \tau_R = \frac{1}{kC_{A_0}^{-n-1}} \] - characteristic reaction time
\[ \tau_m \] - characteristic mixing time
\[ \ell_m \] - characteristic mixing scale

When \( \tau_R \gg \tau_m \), and \( \ell_m \) is small, ideal reactor concepts are useful but even then extremely high conversion cannot be predicted accurately in real reactors unless we have more information on the flow pattern and on the distribution of times that various elements of the fluid reside in the vessel. The concept of Residence Time Distribution (RTD), to be introduced next, is useful here.
When $\tau_m >> \tau_R$ reactor performance completely depends on the scale of mixing $\ell_m$ and mixing intensity ($1 / \tau_m$). If we can describe mixing in the vessel we can describe reaction progress as well. There is another way of looking at the concepts of scale and intensity of mixing by describing the degree of segregation of the fluid and the nature of exchange, or mixing, of all fluid elements that entered together with their environment comprised of all other fluid elements. The former approach is useful in very fast reactions, the outcome of which is completely determined by the turbulent field. The second approach is useful for those reactions the rate of which is comparable or slower to the rate of mixing. Then one can say that

$$\text{Reactor Performance} = \left( \text{kinetics, flow pattern, state of aggregation} \right) \text{ of the fluid and earliness of mixing}$$

(5)

We can now consider the description of the mixing process by two levels: macromixing and micromixing.

- **Macromixing** is a global description of mixing yielding the information on how long various elements of the incoming flow spend in the process vessel.
- **Micromixing** is a more detailed description of mixing on a microscopic level providing the information on the scale of aggregation of the fluid and earliness or lateness of mixing, i.e. on the environment that the individual fluid elements experience in the vessel.
CHARACTERIZATION OF MACROMIXING
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2. CHARACTERIZATION OF MACROMIXING

2.1 Residence Time Distributions, What are they?

In describing a flow pattern in any flow system, reactors in particular, since the hydrodynamic equations of flow are too complex to solve, it is useful to at least provide the information on what is the distribution of residence times for the outflow. Here by residence time we mean the time that a fluid element (particle) spends within the boundaries of the system (reactor). We will first define all the functions that are customarily used to characterize the flow pattern.

2.1.1 Exit Age Density Function, \( E(t) \)

We define a probability density function or exit age density function by

\[
E(t) \, dt = \left( \frac{\text{fraction of the outflow that has resided}}{\text{in the system between time } t \text{ and } t + dt} \right)
\]

(1)

Clearly then \( E(t) \) has units of \( \text{time}^{-1} \)

The key concepts associated with the above are:

1. The flowing fluid contains entities that are conserved. These entities may be molecules, atoms, particles, etc. and from now on we will call these conserved quantities fluid elements.
2. Every fluid element has some original entry point and final departure point from the system.
3. The system consists of a volume in a three dimensional space and there is no ambiguity with regard to its boundaries.
4. Fluid elements have zero age as they enter and acquire age equal to the time spent in the system. Aging stops if the fluid element leaves the system but resumes if the same element returns into the system and stops completely when the element leaves never to return again. At that point its age becomes the residence time of the element in the outflow.

The rules for a probability density function (p.d.f.) require that:

\[
E(t) \geq 0 \text{ on } t \in (0, \infty)
\]

(2)

\[
\int_{0}^{\infty} E(t) \, dt = 1
\]

(3)

Equation (2) simply reminds us that fractions of the outflow of any residence time must be non-negative and that residence time can take only positive values. Equation (3) requires that the sum of all fractions be unity.
2.1.2 Residence Time Distribution, $F(t)$

The RTD, or residence time distribution, can now be defined by

$$F(t) = (\text{fraction of the outflow of residence time less than } t) = \int_0^t E(t) \, dt$$  \hspace{1cm} (4)

and is obtained by summing all the fractions of the outflow between residence time of 0 and $t$. In terms of probability theory, $F(t)$ is the probability that the fluid element of the outflow has residence time less than $t$.

2.1.3 Washout Function, $W(t)$

The so-called washout function, $W(t)$, is the probability that the fluid element in the outflow has residence time larger than $t$; it is the fraction of the outflow of residence times larger than $t$.

$$W(t) = 1 - F(t) = \int_t^\infty E(\tau) \, d\tau$$  \hspace{1cm} (5)

The functions defined so far (i.e. $E(t)$, $F(t)$, $W(t)$) are based on the fluid elements of the outflow as their sample space (population) and characterize the outflow. (How to determine these is a question that we will address later).

2.1.4 Internal Age Density Function, $I(t)$

Let us now consider the fluid elements within the system at some actual time $t_a = 0$ and consider how they are distributed in their ages, the age of an element being the time that elapsed since its entry to the system.

Let us define:

$$I(\alpha) d\alpha = \left( \text{fraction of the fluid elements in the reactor} \right) \text{ that has an age between } \alpha \text{ and } \alpha + d\alpha$$  \hspace{1cm} (6)

where $I(\alpha)$ is the internal age density function. To relate $I(\alpha)$ to the functions already defined we can consider the system at time $\alpha$ and $\Delta \alpha$ seconds later. Make a mass balance on fluid elements around age $\alpha$.

$$\begin{align*}
\text{(Fluid elements in the system of age about } \alpha + \Delta \alpha) & \quad - \\
\text{(Fluid elements in the system of age about } \alpha) & \quad = \\
\text{(Fluid elements fed to the system of age } \alpha \text{ to } \alpha + \Delta \alpha \text{ during time } \Delta \alpha) & \quad - \\
\text{(Fluid elements leaving the system of age } \alpha \text{ to } \alpha + \Delta \alpha \text{ during time } \Delta \alpha) & \quad - \\
\end{align*}$$  \hspace{1cm} (7)

Since elements of any age other than zero cannot be introduced to the system (since age can only be acquired by residing in the system) the first term on the right hand side is zero. The other terms, using the definitions introduced earlier, can be expressed as follows:
\[ VI(\alpha + \Delta \alpha) \Delta \alpha - VI(\alpha) \Delta \alpha = -\frac{Q \Delta \alpha E(\tilde{\alpha}) \Delta \alpha}{\int_0^{\tilde{\alpha}} E(\alpha) d\alpha} \]  

where \( \alpha + \Delta \alpha \geq \tilde{\alpha} \geq \alpha \).

The limit process gives

\[
\lim_{\Delta \alpha \to 0} \frac{I(\alpha + \Delta \alpha) - I(\alpha)}{\Delta \alpha} = -\frac{Q}{V} \lim_{\Delta \alpha \to 0} E(\tilde{\alpha})
\]

\[
\frac{dI}{d\alpha} = -\frac{1}{t} E(\alpha) = -\frac{1}{t} \frac{dF}{d\alpha} = \frac{1}{\bar{t}} \frac{dW}{d\alpha}
\]

The last two equalities in eq. (8) are obtained using the relationship between \( E, F, W \) defined by eqs. (4, 5). We also took the mean residence time to be \( \bar{t} = V/Q \). The boundary condition required to solve eq. (8) is that at \( \alpha \to \infty \) \( I = 0 \) and \( W = 0 \), \( F = 1 \) so that

\[
I(\alpha) = \frac{1}{t} [1 - F(a)] = \frac{1}{\bar{t}} W(\alpha)
\]

### 2.1.5 Mean Residence Time and Mean Age

Now it only remains to be established that the mean residence time, which is indeed the mean or first moment of the \( E \) function, is equal to \( V/Q \).

\[
(\text{mean residence time}) = \sum_t (\text{residence time} \ t \ of \ a \ fluid \ element) \times
\]

\[
(\text{fraction of the elements of residence time} \ t)
\]

\[
\bar{t} = \frac{1}{\bar{t}} \int_0^\infty t \ E(t) \ dt = -\frac{V}{Q} \int_0^\infty \frac{dI}{d\alpha} \ d\alpha = \frac{V}{Q} \left[ -tl \right]_0^\infty + \int_0^\infty I \ dt = \frac{V}{Q}
\]

Using eq (8) a proof given above can readily be established. Indeed \( \bar{t} = V/Q \).

From the definition of the RTD it follows that \( \lim_{t \to 0} I(t) = 0, \lim_{t \to \infty} F(t) = 1 \)

The mean age of the fluid in the vessel by definition is:

\[
\bar{\tau}_f = \int_0^\infty t \ I(t) \ dt = \frac{1}{t} \int_0^\infty t \ dt \int_0^\infty E(\tau) \ d\tau = \frac{1}{t} \int_0^\infty E(\tau) \ d\tau \int_0^\infty t \ dt = \frac{1}{2\bar{t}} \int_0^\infty \bar{\tau}^2 \ E(\tau) \ d\tau
\]

We will see later that we can put to good use the moments of the \( E \) curve defined by:

\[
\mu_n = \int_0^\infty t^n \ E(t) \ dt
\]

We have already seen that \( \mu_0 = 1, \quad \mu_1 = \bar{\tau} \) and, therefore, in terms of the moments of the \( E \)-curve the mean age is
\[ \bar{t}_I = \frac{\mu_2}{2\bar{t}} = \frac{\mu_2}{2\mu_1} \]  

(13)

It is customary to use the variance, \( \sigma^2 \), or the second central moment, which measures the spread of the curve. The central moments are defined by:

\[ \mu_{nc} = \int_0^\infty (t - \mu_1)^n E(t) \, dt \]  

(14)

so that

\[ \mu_2 = \mu_2 - \mu_1^2 = \mu_2 - \bar{t}^2 = \sigma^2 \]  

(15)

Then:

\[ \bar{t}_I = \bar{t} = \frac{\sigma_2^2}{2\bar{t}} = \frac{\bar{t}}{2} \left[ 1 + \frac{\sigma_D^2}{\bar{t}^2} \right] \]  

(15a)

where \( \sigma_D^2 \) is the dimensionless variance, \( \sigma_D^2 = \sigma^2 / \bar{t}^2 \). Often we will use \( \sigma^2 \) for \( \sigma_D^2 \).

### 2.1.6 Ideal Reactors

We can now ask the question as to what the above density and distribution functions look like for ideal reactors.

For a PFR all elements of the outflow have the same residence time equal to the mean residence time.

\[ E_{PFR}(t) = \delta(t - \bar{t}) \]  

(16a)

\[ F(t) = H(t - \bar{t}) \]  

(16b)

\[ W(t) = 1 - H(t - \bar{t}) \]  

(16c)

\[ I(t) = \frac{1}{\bar{t}} \left[ 1 - H(t - \bar{t}) \right] \]  

(16d)

The mean age in the system is \( \bar{t}_I = \frac{\bar{t}}{2} \) since there is no spread of the \( E \) curve around the mean. Then the mean age is equal to half of the mean residence time.

For a CSTR, the age density function is the same as the residence time (i.e. exit age) density function of the outflow since there is perfect mixing, and the probability of exiting does not depend on the age of the fluid element.

\[ E_{CSTR}(t) = I_{CSTR}(t) \]  

(17a)
Using eq (8) this implies
\[ \frac{dI}{dt} = \frac{1}{\bar{t}} I \]  
(18a)

We also know that \( I(t) \) must e a p.d.f. so that
\[ \int_{o}^{\infty} I(t) \, dt = 1 \]  
(18b)

Equations (18a) ad (18b) yield readily:
\[ I_{CSTR}(t) = \frac{1}{\bar{t}} e^{-t/\bar{t}} = E_{CSTR}(t) \]  
(19)
\[ F(t) = 1 - e^{-t/\bar{t}} = 1 - W(t) \]  
(20)
\[ \bar{t}_{r} = \bar{t} \]  
(21)

The mean age of the fluid elements in a perfectly mixed stirred tank is equal to the mean residence time of the exiting fluid. This is to be expected since the assumption of perfect mixing requires that there is no difference between the exit stream and the contents of the vessel.

### 2.1.7 Intensity Function, \( \Lambda(t) \)

The conditional probability density, or the intensity function, \( \Lambda(t) \), is defined as follows:
\[ \Lambda(t) dt = \text{ (fraction of fluid elements in the system of age between } t \text{ and } t + dt \text{ that will exit during the next time interval } dt \text{).} \]

\( \Lambda(t) \) can be determined from the previously defined functions by the following procedure:

\[ V I(t) dt \cdot \Lambda(t) dt = (Q dt) E(t) dt \]  
(22)

\[ \Lambda(t) = \frac{E(t)}{\bar{t} I(t)} = \frac{E(t)}{W(t)} = \frac{E(t)}{1 - F(t)} \]  
(23)
2.1.8 Dimensionless Representation

It is customary to use dimensional time $\theta = t/\bar{t}$. Then the set of function defined over the $\theta$ domain are $E_\theta, F_\theta, I_\theta, \Lambda_\theta$. Since

(Fraction of the fluid of residence time $t$ to $t + dt$) =
(Fraction of the fluid of residence time $\theta$ to $\theta + d\theta$)

$$E(t)dt = E_\theta(\theta)d\theta$$

This implies

$$E_\theta(\theta) = E(t)\frac{dt}{d\theta} = \bar{t}E(\bar{t} \theta)$$

(24)

Equation (24) indicates that if in the functional form for $E(t)$ we substitute $t = \bar{t} \theta$ and multiply the whole function with the mean residence time, $\bar{t}$, we obtain the dimensionless $E_\theta(\theta)$.

Equation (24) is a well known relationship from probability and statistics where it is presented as the general rule for an independent variable change in a p.d.f. We are in fact compressing the independent variable by $1/\bar{t}$ and, hence, we have to expand the ordinate by $\bar{t}$ in order to preserve the area under the curve to be unity i.e. $\int_0^\infty E_\theta(\theta)d\theta = 1$. Similarly, using well known relations from the theory of distributions we can show that

$$F_\theta(\theta) = F(\bar{t} \theta)$$

(25a)

$$I_\theta(\theta) = \bar{t}I(\bar{t} \theta)$$

(25b)

$$W_\theta(\theta) = W(\bar{t} \theta)$$

(25c)

$$\Lambda_\theta(\theta) = \bar{t}\Lambda(\bar{t} \theta)$$

(25d)

**SUMMARY**

**Review:** $E, I, W, F, \Lambda$ and their inter-relationships

$$\frac{dI}{dt} = -\frac{1}{\bar{t}}E = \frac{1}{\bar{t}}\frac{dW}{dt} = -\frac{1}{\bar{t}}\frac{dF}{dt}$$

$$F = \int_0^t E(t)dt = 1 - W$$

$$\Lambda = \frac{E(t)}{\bar{t}I(t)} = \frac{E(t)}{W(t)}$$
\[ \bar{t} = \frac{V}{Q} = \int_{0}^{\infty} tE(t) \, dt \]

\[ \mu_n = \int_{0}^{\infty} t^n E(t) \, dt \quad \sigma_D^2 = \frac{\mu_2 - \mu_1^2}{\mu_1^2} \quad \text{when} \quad \mu_0 = 1 \]

\[ \bar{t}_I = \int_{0}^{\infty} tI(t) \, dt = \frac{\bar{t}}{2} \left[ 1 + \sigma^2 \right] \quad \theta = \frac{t}{\bar{t}} \]

PFR \Rightarrow E = \delta(t - \bar{t}) \quad \text{CSTR} \Rightarrow E(t) = \frac{1}{\bar{t}} e^{-t/\bar{t}} \quad E(t) \, dt = E(\theta) \, d\theta

### 2.2 How to Obtain RTDs or Age Density Functions Experimentally

Experimentally we can obtain directly the exit age density function, \( E(t) \), residence time distribution, \( F(t) \), and internal age density function, \( I(t) \), by using tracers. By injecting, for example, a step input of tracer at time \( t = 0 \) at the inlet of the system we can monitor the distribution of residence times of the tracer elements in the outflow. This information can be inferred from some signal measured in the outflow which is proportional to tracer concentration such as light absorption or transmission, reflection, current, voltage, etc. This output signal can be interpreted in terms of the residence times of the tracer only if:

a) The system is closed, i.e., the tracer enters and leaves the system by bulk flow only, i.e., diffusion or dispersion effects are negligible in the inlet and outlet plane.

b) Tracer injection is proportional to flow, i.e., at the inlet boundary tracer injection rate is proportional to the velocity component normal to the boundary at each point of the boundary.

c) The total rate at which the tracer leaves the system is the integral of the product of the velocity times concentration integrated in a vectorial sense over the whole exit boundary.

In addition, the residence time distribution of the tracer will yield the residence time distribution for the carrier fluid, which is what we want, if and only if:

a) the system is at steady state except with respect to (w.r.t.) the tracer concentration;

b) the system is linear, i.e., the response curve is proportional to the mass of tracer injected;

c) the tracer is perfect, i.e., behaves almost identically to the carrier fluid;

d) there is a single flowing phase and single homogeneous phase within the system;

e) the system has one inlet and outlet;

f) tracer injection does not perturb the system.

Under the above set of conditions we can interpret the response to a step-up tracer injection to directly obtain the \( F \) curve for the carrier fluid. Suppose we had no tracer in the inlet stream (white fluid), and
then at time $t = 0$ we started injecting the tracer (red fluid) at such a rate that its concentration at the inlet is $C_o$. The quantity of tracer elements injected per unit time is $Q C_o$. For each tracer element there are $K$ carrier fluid elements that, if tracer is perfect, behave identically to the red elements of the tracer. Hence, $K Q C_o$ white fluid elements are entering the system per unit time. We monitor at the outlet tracer concentration $C$. At each time $t$ all the red elements that we see at the outlet, $QC$, have residence times less than $t$ because they only could have entered the system between time 0 (when tracer injection started) and time $t$. For each red element of residence time $t$ there must be $K$ white elements of carrier fluid that have the same residence time since they entered with these red elements and have behaved in the same manner. By definition

$$F(t) = \frac{\text{(fraction of the outflow of residence times less than } t)}{\text{(total elements of the outflow)}}$$

$$= \frac{\text{(tracer elements) + (carrier fluid elements of the same residence time)}}{\text{(total elements of the outflow)}}$$

$$= \frac{QC + KQC}{(1 + K)QC_o}$$

The denominator above results from a simple mass balance. Per unit time we feed into the system $QC_o$ tracer elements and $K QC_o$ carrier fluid elements. Total rate of input must be equal to the total rate of output which, therefore, is $(1 + K) QC_o$. Then the RTD of the carrier fluid is given by

$$F(t) = \frac{C(t)}{C_o}$$

(26)

The $E$, $W$, $I$ curves can now be evaluated from the RTD (i.e., the $F$ curve) by previously reported relationships.

The residence time density function, $E(t)$, can also be obtained directly from an impulse tracer injection. During a short time interval $dt$ at $t = 0$ we inject a pulse of $m_T$ of tracer elements (and of course for each tracer element $K$ carrier fluid elements entered). At the outlet we monitor tracer response $C$. During time period $dt$ at time $t$ we collect $QC dt$ tracer elements and $KQC dt$ elements of the carrier fluid of the same residence time. All these elements have residence time between $t$ and $t + dt$ because they entered the system between time 0 and $dt$. By definition:

$$E(t) dt = \text{(fraction of the outflow of residence time between } t \text{ and } t + dt)$$

$$= \frac{\text{elements of the outflow of residence time between } t \text{ and } t + dt}{\text{between } t \& t + dt \text{ collected during interval } dt}$$

$$= \frac{\text{elements of the outflow of residence time between } t \text{ and } t + dt}{\text{(total elements collected during } dt)}$$

(Updated 01/05)
(tracer elements in the outflow collected during time $dt$ at $t$) +

\[
= \frac{Q C dt + K Q C dt}{m_r + K m_r}
\]

\[
E(t) dt = \frac{Q C dt (1+K)}{m_r (1 + K)}
\]

\[
E(t) = \frac{Q C}{m_r}
\]

(27)

Other functions $F$, $I$, $W$ can now be derived from the $E$ curve using previously reported relationships.

The total mass balance on tracer in a pulse injection requires that all the tracer injected must eventually emerge, which is the same as requiring that \( \int_{0}^{\infty} E(t) dt = 1 \). This formula is used to check the tracer mass balance and ensure that the experiment is executed properly. The formula can also be used (when one is confident that tracer is indeed conserved) to determine the unknown flow rate:

\[
Q = \frac{m_r}{\int_{0}^{\infty} C(t) dt}
\]

(28)

Whenever the mass balance for the tracer is not properly satisfied the tracer test does not represent a proper way of determining the $E$ curve. Various pitfalls were discussed by Curl, R. and McMillan, M. L. (AIChE J., 12, 819, 1966).

The washout curve, $W(t)$, can of course be obtained from the step-up tracer test by subtracting the $F(t)$ curve from unity, $W = 1 - F$. This produces inaccurate results at large times because of subtraction of numbers of the similar order of magnitude since $\lim_{t \to \infty} F = 1$. Therefore, $W(t)$ can be obtained directly by a step-down tracer test. Imagine that at the end of the step-up test both the inlet and exit tracer concentration are $C_o$. Now at $t = 0$ we start the stop watch and reduce the inlet tracer concentration to 0. Then all the tracer elements appearing at the outflow at time $t$ are older than $t$ since they have entered the system before time 0. Due to linearity and perfect behavior of the tracer, for each tracer element there are $K$ carrier fluid elements of the same residence time. By definition:

\[
W(t) = \text{(fraction of the outflow that has residence times larger than $t$)} = \frac{(1+K)QC}{(1+K)QC_o} \frac{C}{C_o}
\]

(29)

The area under the washout curve gives the mean residence time:
Based on the previously derived relationships you should be able to prove the above. The $I(t)$ curve can be evaluated readily using the step-down tracer test, its integral and eq (31):

$$I(t) = \frac{1}{t} \int W(t) \, dt$$  

(31)

The $I(t)$ curve is often determined directly in biomedical applications by injecting a pulse of tracer $m_{\tau_0}$ at time 0, and by monitoring the response of the whole system (not the outflow) which is proportional to the mass of tracer remaining at time $t$, $m_{\tau}$. Then:

$$I(t) = \frac{m_{\tau}(t)}{m_{\tau_0}}$$  

(32)

Some Other Items of Interest:

Perfect tracer - detectable, yet same behavior as carrier fluid and at infinite dilution.

Radioactive tracers - half life $\gg \tilde{t}$ (only exception positron emitters).

Electrolytes - conductivity meters (cast epoxy tubular body carbon ring electrodes and female pipe threaded ends with a self balancing bridge working at 1000 Hz to eliminate polarization).

Dyes - colorimetric detectors and spectrophotometer may give nonlinear response.

- thermal conductivity detectors.
- flame ionization detectors (organics)
- $R$ ($CO_2$, $SO_2$, $NH_3$ in mixture of diatomic gases) two channel design preferred.

2.3 How To Derive Age Density Functions

We know what the age density functions for the two ideal reactors (PFR and CSTR) look like. Using these we can derive the age density functions for a generalized compartmental model with time lags. By this we mean that if we have evidence or reason to believe that a real flow system or reactor can be represented by a set of CSTR's (well mixed compartments) and PFR's (time lags) in series or parallel we can readily derive an $E$ curve for any such combination.

Here, and in later applications, it is very useful to use Laplace transforms defined by
\[
\overline{E}(s) = L\{E(t)\} = \int_{0}^{\infty} e^{-st} E(t) \, dt
\]  

(33)

Any network of CSTR's and PFR's consists of: elements in parallel, elements in series, split points and mixing points (where points are considered to have no volume). The rules for dealing with these are explained below.

2.3.1 Systems in Parallel

Consider two parallel branches represented above. The top branch contains the fraction \(\beta\) of the total volume of the system and the bottom branch has \((1-\beta)\) of the total volume. The splitting point \(S\) and mixing point \(M\) have no volume. Let the transfer function (Laplace transform of the unit impulse response and hence the Laplace transform of the residence time density function, \(E\)) of the top branch be \(\overline{E}_1(s)\), if that branch had all the volume of the system and all the flow passed through it. Let \(\overline{E}_2(s)\) be the Laplace transform (LT) of the impulse response of the bottom branch if all the volume was in it and all the flow ran through it. Since only volume \(\beta V\) is in the upper branch and \(\alpha Q\) flow rate passes through it, the LT of the response is \(\overline{E}_1 \left( \frac{\beta}{\alpha} s \right)\) and similarly for the bottom branch \(\overline{E}_2 \left( \frac{1-\beta}{1-\alpha} s \right)\). The overall response is obtained by the weighted average of the two, where at point \(M\) the weighting is accomplished proportionally to flow.

\[
\overline{E}(s) = \alpha \overline{E}_1 \left( \frac{\beta}{\alpha} s \right) + (1-\alpha) \overline{E}_2 \left( \frac{1-\beta}{1-\alpha} s \right)
\]  

(34)

This can readily be generalized to \(M\)-branches in parallel

\[
\overline{E}(s) = \sum_{j=1}^{M} \alpha_j \overline{E}_j \left( \frac{\beta_j}{\alpha_j} s \right)
\]  

(35)

where \(\alpha_j\) is the fraction of the total flow rate going through branch \(j\) and \(\beta_j\) is the fraction of the total volume of the system that is in branch \(j\).
We build block diagrams for flow pattern representation out of two ideal patterns (plug flow and complete backmixing) or their combinations. We know the $E_{\theta}(\theta)$ curves for our building blocks with $\theta = t/i$ where $i$ is the total mean residence time. They are the impulse responses of a PFR and a CSTR. If the building block is a subsystem then the mean residence time is $\tilde{t}_{sub} = \frac{\beta}{\alpha} t$ ($\beta$ = fraction of total system's volume present in subsystem, $\alpha$ - multiple or fraction of total system's throughput that flows through the subsystem) so that $\theta_{sub} = t/\tilde{t}_{sub} = \frac{\alpha t}{\beta i} = \frac{\alpha}{\beta} \theta$. Then the subsystem's dimensionless impulse response is: $E_{\theta}(\frac{\alpha}{\beta} \theta)$.

More generally speaking we are stating that if the dimensionless response of a system with volume $V$ and flow rate $Q$ that exhibits a certain flow pattern is $E_{\theta}(\theta)$, then the impulse response of the same system when it is a subsystem, i.e. a building block within a larger system) (containing fraction $\beta$ of the volume of the whole system and with flow rate of $\alpha Q$ going through it) is given by $E_{\theta}(\frac{\alpha}{\beta} \theta)$.

The dimensional impulse response of the subsystem then is given by

$$E_{\theta}(\theta_{sub}) d \theta_{sub} = E_{sub}(t) dt \tag{36}$$

When $\alpha = \beta = 1$ we get the whole system's response.

$$E(t) = \frac{1}{t} E_{\theta}(t/i) \tag{37}$$

Thus, by replacing $i$ by $\frac{\beta}{\alpha} t$ we get $E_{sub}(t)$ from $E(t)$. Now the previously stated relation for the Laplace transforms follows.

$$L\{E(t)\} = \int_0^\infty e^{-st} E(t) dt = \frac{1}{t} \int_0^\infty e^{-s/t} E_{\theta}(t/i) dt = \overline{E}(s) \tag{38}$$

$$L\{E_{sub}(t)\} = \frac{\alpha}{\beta i} \int_0^\infty e^{-s/t} E_{\theta}(\frac{\alpha t}{\beta i}) dt = \frac{1}{\beta i} \int_0^\infty e^{-\frac{\beta t}{\alpha}} E_{\theta}(\frac{u}{i}) du = \overline{E}_{sub}(\frac{\beta}{\alpha} s) \tag{39}$$

by replacing $s$ with $\frac{\beta}{\alpha} s$ in $\overline{E}(s)$ we get $\overline{E}_{sub}$.

Also:

$$L\{E_{\theta}(\theta)\} = \int_0^\infty e^{-st} E_{\theta}(\theta) d\theta = \overline{E}_{\theta}(s) \tag{40}$$
\[
L \{E_{\theta_{\alpha\theta}}(\theta)\} = \int_{\alpha}^{\beta} e^{-\theta} \theta e^{-\theta} \alpha E_{\theta_{\alpha\theta}}(\theta) d\theta = \frac{\beta}{\alpha} \int_{\alpha}^{\beta} E_{\theta_{\alpha\theta}}(\theta) d\theta = \frac{\beta}{\alpha} E_{\theta_{\alpha\theta}} \left( \frac{\beta}{\alpha} \right)
\]  
(41)

However the mean of \( E_{\theta_{\alpha\theta}} \) is not 1 but \( \frac{\beta}{\alpha} \).

**Example**

1. 2-CSTR's of different volume in two parallel branches:

\[
Q_1 + Q_2 = Q  \\
\alpha = \frac{Q_1}{Q}  \\
V_1 + V_2 = V  \\
\beta = \frac{V_1}{V}
\]

Now \( \bar{E}(s) = \alpha \bar{E}_1(\frac{\beta}{\alpha}s) + (1 - \alpha) \bar{E}_2(\frac{1 - \beta}{1 - \alpha} s) \)

where \( \bar{t}_i = \frac{\beta}{\alpha} t, \bar{t}_2 = (1 - \beta) \frac{1}{1 - \alpha} t \)

\[
\bar{E}_1(s) = \bar{E}_2(s) = \frac{1}{1 + \bar{t}_i s} ; \quad i = 1 \text{ or } 2
\]

\[
\bar{E}(s) = \alpha \frac{1}{1 + \frac{\beta}{\alpha} \bar{t} s} + (1 - \alpha) \frac{1}{1 + \frac{1 - \beta}{1 - \alpha} \bar{t} s}
\]

\[
E(t) = L^{-1} \{ \bar{E}(s) \} = \frac{\alpha}{\beta \bar{t}} e^{-\frac{\alpha t}{\beta \bar{t}}} + (1 - \alpha) e^{-\frac{(1 - \alpha) t}{(1 - \beta) \bar{t}}}
\]

2.3.2 *Systems in Series*

Let us now consider a system in series consisting of two elements as shown below.
Let the transfer function of the first one be \( E_1(s) \) and of the second one \( E_2(s) \). If the first one contains a fraction \( \beta \) of the total volume of the system then the system’s response in the Laplace domain (transfer function) is given by

\[
\bar{E}(s) = E_1(\beta s) \times E_2((1-\beta)s)
\]  

(42)

In time domain this is:

\[
E(t) = \int_0^t \frac{1}{\beta} E_1 \left( \frac{\tau}{\beta} \right) \frac{1}{1-\beta} E_2 \left( \frac{t-\tau}{1-\beta} \right) d\tau
\]  

(43)

This is the well known convolution theorem for linear systems.

The above rule can be readily generalized to \( N \) subsystems in series, each containing a fraction \( \beta_j \) of the total volume of the system. The overall transfer function is given by

\[
\bar{E}(s) = \prod_{j=1}^{N} \bar{E}_j(\beta_j s)
\]  

(44)

where \( \bar{E}_j(s) \) is the Laplace transform of the impulse response of the \( j \)-th individual subsystem as if it contained the whole volume of the system.

**Example:**

Find the E-curve of \( N \)-equal sized CSTRs in series.

We know that for a single stirred tank of volume \( V \) and with flow rate \( Q \) the impulse response is given by

\[
E_1(t) = \frac{1}{\tau} e^{-\frac{t}{\tau}}
\]

so that the transfer function is

\[
\bar{E}_1(s) = \frac{1}{1 + \frac{s}{\tau}}
\]

where \( \tau = V / Q \)

For \( N \) equal size stirred tanks in series each tank contains \( \beta_j = \frac{1}{N} \) fraction of the total volume. Hence

\[
\bar{E}_j(\beta_j s) = \bar{E}_j \left( \frac{s}{N} \right) = \frac{1}{1 + \frac{\tau}{N} s}
\]
The overall transfer function is obtained by eq (44):

\[ \bar{E}(s) = \prod_{j=1}^{N} \frac{1}{1 + \frac{j}{N}s} = \frac{1}{\left(1 + \frac{1}{N}s\right)^N} \]

The overall impulse response then is obtained by inversion of the Laplace transform

\[
E(t) = L^{-1}\left\{ \frac{1}{\left(1 + \frac{1}{N}s\right)^N} \right\} = \left(\frac{N}{\bar{t}}\right)^N L^{-1}\left\{ \frac{1}{s + \frac{N}{\bar{t}}} \right\} = \left(\frac{N}{\bar{t}}\right)^N \frac{\bar{t}^{N-1}}{(N-1)!} e^{-N\bar{t}/\bar{t}}
\]

The dimensionless E-curve is

\[ E_\theta(\theta) = \bar{t}E(\bar{t}\theta) = \frac{N^N}{(N-1)!} \theta^{N-1} e^{-N\theta} \]

We can now use the above to derive the responses of N-CSTR's of equal size in series, CSTR's and PFR's in parallel and systems with recycle.

In the example on nonideal stirred tank that follows the section on systems with recycle we will show how to determine the parameters of the model from the experimentally determined E-curve and how to use this in assessing reactor performance.
2.3.3 Systems with Recycle

Once you have mastered the derivation of the transfer function for subsystems in series and subsystems in parallel, you should be able to handle systems with recycle. The only new “rule” is the splitting rule where by if you split a stream each of the outgoing streams possesses the same transfer function.

Let us consider a general recycle system depicted below:

Flow rate $Q$ flows through a recycle system (the system within the dashed box is the system with recycle) of total volume $V$. Internally, at point $M$ flow rate $Q$ is joined by recycle flow rate, $RQ$, so that the flow rate of $(R+1)Q$ flows through the forward branch of the system that contains volume $\beta V$. At splitting point $S$, $RQ$ is recycled through the recycle branch of volume $(1-\beta)V$ which flow rate $Q$ leaves the system. The transfer function of the forward branch is $G_1$ (we mean by it $\frac{\beta s}{s + 1}$). The transfer function of the recycle flow branch is $G_2$ i.e. $\frac{(1-\beta)s}{s + 1}$. The transfer function of the total system is $E(s)$.

Applying what we have learned so far, we note that for a normalized impulse injection of $\delta(t)$ the transfer function for the inlet is 1. The mass balance in the Laplace domain yields

$$\left(1 + R G_2 E\right)G_1 = (R + 1)E$$

This response $(R + 1)E$ is obtained by the product (i.e. convolution in the time domain) of the transfer function for the forward path, $G_1$, and the transfer function for the inlet stream after mixing point $M$. The later is the sum of the transfer function for the fresh inlet stream (i.e. 1) and the product (i.e. convolution in time domain) of the transfer function for the recycle branch, $G_2$, and the transfer function for the exit stream, $E$, multiplied by $R$ due to flow rate being $RQ$.

We can now solve eq (45) for the transfer function of the system $E$:

$$E = \frac{G_1}{R + 1 - R G_1 G_2}$$

(46a)
Which can also be written as:

\[
\bar{E} = \frac{1}{R+1} \cdot \frac{\bar{G}_1}{1 - \frac{R}{R+1} \cdot \bar{G}_1 \cdot \bar{G}_2}
\]  

(46b)

We recall that \(\bar{G}_1, \bar{G}_2\) are functions of \((\beta s/R + 1)\) and \((1 - \beta)s/R\), respectively.

To get the impulse response in the time domain, inversion of equation (46a) or (46b) can be attempted using the usual rules for Laplace transform inversion.

Often it is necessary to expand equation 46(b) by binomial theorem to get:

\[
\bar{E} = \frac{1}{R+1} \sum_{n=0}^{\infty} \left( \frac{R}{R+1} \right)^n \bar{G}_1^n \cdot \bar{G}_2^n
\]  

(47)

Which can be rearranged to the following form:

\[
\bar{E} = \frac{1}{R} \sum_{n=0}^{\infty} \left( \frac{R}{R+1} \right)^n \bar{G}_1^n \cdot \bar{G}_2^{n-1}
\]  

(48)

To obtain the impulse response in the time domain one can now invert the series in equation (48) term by term.

**Example**

Consider a recycle system with volume \(\beta V\) in the forward branch and volume \((1 - \beta)V\) in the recycle branch as sketch below. Plug flow occurs in both branches so that

\[
\bar{G}_1 = e^{-\beta \frac{i \pi s}{R+1}}
\]

\[
\bar{G}_2 = e^{-(1 - \beta)i \pi s/R}
\]

According to equation (48)

\[
\bar{E} = \frac{1}{R} \sum_{n=1}^{\infty} \left( \frac{R}{R+1} \right)^n e^{\frac{\beta i \pi n}{R+1}} e^{-(1 - \beta)i \frac{n-1}{R} \pi}
\]

Inversion, term by term, yields

\[
E(t) = \frac{1}{R} \sum_{n=1}^{\infty} \left( \frac{R}{R+1} \right)^n \delta \left( t - \frac{\beta i n}{R+1} - \frac{(1 - \beta) \frac{n-1}{R} \pi}{R} \right)
\]
Let us write out explicitly the first three terms

\[ E(t) = \frac{1}{R+1} \delta(t - \frac{\beta \bar{t}}{R+1}) + \frac{R}{(R+1)^2} \delta\left(t - \frac{2\beta \bar{t}}{R+1} - \frac{(1-\beta)\bar{t}}{R}\right) + \frac{R^2}{(R+1)^3} \delta\left(t - \frac{3\beta \bar{t}}{R+1} - \frac{2(1-\beta)\bar{t}}{R}\right) + \ldots \]

This response looks as shown below:

```
<table>
<thead>
<tr>
<th>t</th>
<th>E(t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t_{a1}</td>
<td>1/(R+1)</td>
</tr>
<tr>
<td>t_{a2}</td>
<td>R/(R+1)^2</td>
</tr>
<tr>
<td>t_{a3}</td>
<td>R^2/(R+1)^3</td>
</tr>
</tbody>
</table>
```

Where

\[ t_{a1} = \frac{\beta \bar{t}}{R+1} \]
\[ t_{a2} = \frac{2\beta \bar{t}}{R+1} + \frac{(1-\beta)\bar{t}}{R} \]
\[ t_{a3} = \frac{3\beta \bar{t}}{R+1} + \frac{2(1-\beta)\bar{t}}{R} \]
\[ t_{a_n} = \frac{n\beta \bar{t}}{R+1} + \frac{(n-1)(1-\beta)\bar{t}}{R} \]

Now, mentally perform a tracer experiment in which you injected normalized mass of tracer of unity (i.e. \(m_T/Q = 1\)). The first time the tracer appears at the exit is at \(t_{a1} = \beta \bar{t}/(R+1)\), which is the time it takes to transverse volume \(\beta V\) at flow rate \((R+1)Q\). (Recall \(\bar{t} = V/Q\) always!). The tracer is carried by \((R+1)Q\), only \(Q\) exits and \(RQ\) is recycled. So the amount of tracer carried out by the outflow at \(t_{a1}\) is \(1/(R+1)\). Hence \(1/(R+1)\) is the area under that delta function at \(t_{a1}\).

For the tracer to appear the second time, it must transverse the volume in the recycle branch \(((1-\beta)V\) at flow rate \(RQ\), which takes \((1-\beta)V/RQ\) and then transverse to forward branch again, which takes
another \( t_{a_1} \). So \( t_{a_2} = 2 t_{a_1} + \frac{(1 - \beta) V}{R} \). The amount of tracer that now arrives at the exit is \( \frac{R}{R+1} \) (remember \( 1/(R+1) \) left at the first passage time) and again only the fraction \( \frac{1}{R+1} \) is recycled. So the area under the second delta function at \( t_{a_2} \) is \( \frac{R}{(R+1)^2} \). The rest follows by analogy.

We note that if we had only the response curve we could tell how much volume the recycle system has associated with the forward and recycle branch. The difference

\[
t_{a_n} - t_{a_{n-1}} = \frac{\beta \bar{V}}{R + 1} + \frac{(1 - \beta) \bar{V}}{R} = \text{const}
\]

Since \( t_{a_1} = \frac{\beta \bar{V}}{R + 1} \)

We know that if

\[
t_{a_n} - t_{a_{n-1}} = t_{a_1}
\]

All the volume is in the forward stream i.e. \( \beta = 1 \), Otherwise

\[
t_{a_n} - t_{a_{n-1}} - t_{a_1} = \frac{(1 - \beta) \bar{V}}{R}
\]  

\((*)\)

By dividing the areas under the first peak \( A_1 = \frac{1}{R + 1} \) with the area under the second peak \( A_2 = \frac{R}{(R + 1)^2} \)

we get

\[
\frac{A_1}{A_2} = \frac{R + 1}{R}
\]

\((**)\)

We can use eqs \((*)\) and \((**)\) to get estimates for \( \beta \) and \( R \).
Example of a Nonideal Stirred Tank Reactor

A reactor of volume \( V = 25 \text{ m}^3 \) (25,000 lit) with flow rate \( Q = 1000 \text{ lit/min} = 1 \text{ m}^3/\text{min} \) which was designed to operate as a CSTR and give very high conversion for a 2nd order irreversible reaction \( (A \rightarrow \text{product}) \) is operating poorly at \( x_A = 0.75 \). A pulse of \( m_i = 250 \text{g} \) of tracer is injected instantaneously into the reactor. At the outlet the following exit concentration is measured for the tracer. Initially rapid fluctuations within the first five seconds of very high tracer concentration are observed. Afterwards the following data is obtained:

<table>
<thead>
<tr>
<th>( t ) (min)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c ) (mg/lit)</td>
<td>6.21</td>
<td>3.52</td>
<td>2.15</td>
<td>1.10</td>
<td>0.70</td>
<td>0.40</td>
<td>0.23</td>
<td>0.13</td>
</tr>
</tbody>
</table>

a) How can we model the old reactor?

b) If we had a perfect CSTR what volume do we need for \( x_A = 0.75 \)?

c) What volume of a perfect CSTR do we need to get conversion that currently is produced by the well mixed region?

The rapid initial rise of tracer concentration in the outflow seems to suggest bypassing. The slope of \( \ln c \) vs \( t \) is

\[
\text{slope} = -\frac{\ln \left(1.06 / 0.01 \right)}{85} = -0.0549
\]

We cannot a priori discard the possibility of stagnancy either. Use Cholette and Cloutier model schematically presented in the figure below.

\[ V_m = \text{volume of a perfectly mixed region (CSTR)} \]

\[ V_d = \text{‘dead’ volume, not accessible to flow} \]

Let \( V_m = \beta V \) where \( V = V_m + V_d \).

Fraction of the flow that bypasses is \( (1-\alpha) \). Then the transfer function for the above system is given by

\[
\bar{E} = 1 - \alpha + \frac{\alpha}{1 + \frac{\beta}{\alpha} t_s}
\]

and the impulse response is:
\[ E(t) = (1 - \alpha) \delta(t) + \frac{\alpha^2}{\beta t} e^{\frac{\alpha t}{\beta t}} \]

where \( \tilde{t} = \frac{V}{Q} \).

If we recognize that \( C(t) = \frac{m_i E(t)}{Q} \), then:

\[
C(t) = \frac{m_i}{Q} \left( (1 - \alpha) \delta(t) + \frac{\alpha^2}{\beta t} e^{\frac{\alpha t}{\beta t}} \right)
\]

If we plot on semilog paper

\[
\ln C = \ln \left( \frac{m_i (\alpha^2)}{Q \beta t} \right) - \frac{\alpha}{\beta t} t, \text{ then } \text{slope} = 0.055 = \frac{\alpha}{\beta t} |\text{slope} = |S|
\]

Extrapolation of the exponential to \( t = 0 \) gives

\[
I = C_{\exp}(0) = \frac{m_i (\alpha^2)}{Q \beta t} = 10.7 (mg/L) = 10.7 \times 10^{-3} (g/L)
\]

\[
\frac{C_{\exp}(0)}{|S|} = \frac{m_i (\alpha)}{Q} = \frac{I}{|S|}
\]

\[
\alpha = \frac{Q}{m_i} \frac{I}{|S|}
\]

\[
\alpha = \frac{Q}{m_i} \frac{C_{\exp}(0)}{|S|} = \frac{1000}{250} \frac{10.7 \times 10^{-3}}{0.055} = 0.778
\]

\[
\alpha \approx 0.78
\]

\[ 1 - \alpha = 0.22 \text{ of the flow bypasses the vessel} \]

From the information given we have the mean residence time:

\[ \tilde{t} = \frac{25}{1} = 25 \text{ min} \]

Hence, we can find now the fraction of the total volume, \( \beta \), that is actively mixed.

\[
\frac{\alpha}{\beta t} = 0.055 \quad \beta = \frac{\alpha}{0.055 \tilde{t}} = \frac{0.78}{0.055 \times 25} = 0.567 \approx 0.57
\]

\[
\beta \approx 0.57
\]

\[
V_{\text{active}} = 0.57 \times 25 = 14.25 \text{ m}^3
\]

\[
V_{\text{dead}} = 10.75 \text{ m}^3
\]

Now we need to set the CSTR design equation in order to find the unknown rate parameters:
\[
\frac{V_{\text{active}}}{Q_{\text{active}}} = \frac{\beta V}{(\alpha)Q} = \frac{C_{Ao}x_{Ar}}{kC_{Ao}^2 (1 - x_{Ar})}
\]

Now \( x_{Ar} \) is the actual conversion produced by the reactor found in the stream leaving the active section of the reactor before mixing with the bypass stream

\[
kC_{Ao} = \frac{x_{Ar}}{(1 - x_{Ar})^2} \frac{\alpha}{\beta t}
\]

However, we must first relate this conversion \( x_{Ar} \) to the conversion produced by the reactor as a whole. This requires a balance around the mixing point \( M \). The stream \( \alpha Q \) arriving from the reactor has conversion \( x_{Ar} \), the stream bypassing the reactor has conversion of zero. This balance can be represented by:

\[
(1 - \alpha)F_{Ao} + \alpha F_{Ao} (1 - x_{Ar}) = F_{Ao} (1 - x_A)
\]

\[
1 - \alpha + \alpha(1 - x_{Ar}) = 1 - x_A
\]

\[
1 - \alpha x_{Ar} = 1 - x_A \text{ so that } x_{Ar} = \frac{x_A}{\alpha}
\]

We are told that \( x_A = 0.75 \). Then, for \( x_A = 0.75 \) and \( \alpha = 0.78 \)

\[
x_{Ar} = \frac{0.75}{0.78} = 0.96
\]

\[
kC_{Ao} = \frac{0.96}{(1 - 0.96)^2} \frac{0.78}{0.57 \times 25} = 32.8 \text{ (min}^{-1})
\]

Recall that \( V = \frac{Qx_A}{kC_{Ao} (1 - x_A)} \), Then

\[
V_{\text{new}} (x_A = 0.75) = \frac{1,000 \times 0.75}{32.8 (1 - 0.75)^2} = 366 \ (\text{lit}) = 0.37 \ m^3
\]

b) \[
V_{\text{new}} (x_A = 0.75) = \frac{1000 \times 0.96}{32.8 (1 - 0.96)^2} = 18,293 \ text{lit} = 18.3 \ m^3
\]

c) \[
V_{\text{new}} (x_A = 0.96) = \frac{1000 \times 0.96}{32.8 (1 - 0.96)^2} = 18,293 \ text{lit} = 18.3 \ m^3
\]
2.3.4 Bypassing and Stagnancy

Let us consider now a single CSTR with bypassing. If the portion of the flow that bypasses is \((1 - \alpha)\) the schematic of the system is as follows:

![Bypassing CSTR Diagram](image)

and the impulse response and its transform are given below by eqs. (48) and (49). We expand the transform (see eq (49)) to evaluate its moments, and we tabulate below the dimensionless variance of the system as a function of the fraction of flow that bypasses which is \((1 - \alpha)\). Clearly, the dimensionless variance is larger than one for a CSTR with bypassing indicating pathological behavior.

\[
E(t) = (1 - \alpha) \delta(t) + \frac{\alpha^2}{t} e^{-\alpha t/t}
\]  \hspace{1cm} (49)

\[
\bar{E}(s) = 1 - \alpha + \frac{\alpha}{1 + \frac{s}{\alpha}} = 1 - \alpha + \alpha \left(1 - \frac{t}{\alpha s} + \frac{t^2}{\alpha^2 s^2}\right) = 1 - \tilde{t}s + \frac{\tilde{t}^2}{s^2} + O(s^3)
\]  \hspace{1cm} (50)

By a simple technique that is illustrated later, we have evaluated the moments from the above Laplace transform expansion as:

\[
\mu_0 = 1
\]

\[
\mu_1 = \tilde{t}
\]

\[
\mu_2 = \frac{2\tilde{t}^2}{\alpha}
\]

\[
\sigma^2_E = \frac{2\tilde{t}^2}{\alpha} - \tilde{t}^2 = \frac{\tilde{t}^2 (2 - \alpha)}{\alpha}
\]

\[
\sigma^2_E = \frac{\sigma^2_E}{\tilde{t}^2} = \frac{2 - \alpha}{\alpha}
\]

<table>
<thead>
<tr>
<th>(1 - \alpha)</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma^2_E)</td>
<td>1</td>
<td>1.22</td>
<td>1.5</td>
<td>1.86</td>
<td>2.33</td>
<td>3</td>
<td>4</td>
<td>5.67</td>
<td>9</td>
<td>19</td>
</tr>
</tbody>
</table>

Now let us consider a single CSTR with 'dead' volume. Such dead volume cannot be reached by tracer or by reactant molecules.

![Dead Volume CSTR Diagram](image)
Let $V_d = \beta V$, so $\beta$ is the fraction of the total reactor volume that is for all practical purposes inaccessible. Now the impulse response of the system is:

$$E(t) = \frac{1}{(1 - \beta)V} e^{\frac{-t}{(1-\beta)V}}$$

and its Laplace transform is

$$E(s) = \frac{1}{1 + (1 - \beta)\bar{V} s} = 1 - (1 - \beta)\bar{V} s + (1 - \beta)^2 \bar{V}^2 s^2 + O(s^3)$$

Recall that

$$E(s) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \mu_n s^n$$

Hence,

$$\mu_0 = 1$$

$$\mu_1 = (1 - \beta)\bar{V}$$

$$\mu_2 = 2(1 - \beta)^2 \bar{V}^2$$

$$\sigma_E^2 = \frac{\mu_2 - \mu_1^2}{\mu_1^2} = 1$$

Now we detected the presence of dead volume not from the value of the variance but from the fact that $\mu_1 < \bar{V}$, i.e. the central volume principle is violated. We may note, however, that the central volume principle is never violated and, while a fraction $\beta$ of the volume of the system may be difficult to reach, i.e. is relatively "stagnant", as long as that volume is a physical part of the flow system under consideration it is never "dead", i.e. it will be reached by at least a few elements of the fluid and, hence, elements of the tracer if not by flow then at least by diffusion. The fascinating feature of the central volume principle, which is little known, is that the zeroth moment of the tracer impulse concentration at any point of a closed system is constant and equal to $m_T/Q$ where $m_T$ is the mass of the instantaneous tracer injection and $Q$ is the volumetric flow rate through the system. This means that the area under the concentration response to an impulse injection is constant anywhere in the system (i.e. at all points of the system) and it implies that at points where the tracer concentration response rises rapidly, high values will be of short duration, while where the response is barely detectable, it lasts seemingly forever! This makes sense, as it says that if a point is readily accessible and easy to get to, it is also easy to get out of and the converse is also true - if it is hard to get to a point it is equally hard to get out. With this in mind let us say that our system has a stagnancy.
\[ V_d = \beta V \] which exchanges its contents very slowly with the main well mixed region \( V_m \) at a rate \( \alpha Q \) with \( \alpha \leq 1 \).

By setting up differential mass balances for the tracer in region \( V_m \) and \( V_d \), normalizing tracer concentrations in \( V_m \) and \( V_d \) by multiplying with \( Q/m \) to get the impulse response, and by applying the LaPlace transform and solving the equations in the LaPlace domain you should be able to show that

\[
\bar{E}(s) = \frac{1 + \frac{\beta}{\alpha} \tilde{t}s}{1 + \left( 1 + \frac{\beta}{\alpha} \right) \tilde{t}s + \frac{\beta(1-\beta)}{\alpha} \tilde{t}^2 s^2} \tag{55}
\]

By expanding the denominator via binomial series, multiplying the result with the numerator and grouping items with equal power of \( s \) you should be able to get:

\[
\bar{E}(s) = 1 - \tilde{t}s + \left( 1 + \frac{\beta^2}{\alpha} \right) \tilde{t}^2 s^2 + 0(s^3) \tag{56}
\]

From the above series we readily identify the moments of the E-curve

\[ \mu_0 = 1 \] \hspace{1cm} (57a)
\[ \mu_1 = \tilde{t} \] \hspace{1cm} (57b)
\[ \mu_2 = 2 \left( \frac{\beta^2}{\alpha} + 1 \right) \tilde{t}^2 \] \hspace{1cm} (57c)

Hence the dimensionless variance of the E-curve is

\[ \sigma_E^2 = \frac{\mu_2 - \mu_1^2}{\mu_1^2} = 1 + 2 \frac{\beta^2}{\alpha} > 1 \] \hspace{1cm} (58)

Clearly no matter what volume fraction \( \beta \) is relatively stagnant, the dimensionless variance is always greater than one. The quantity \( \sigma_E^2 - 1 \) is proportional to the square of the stagnant volume fraction and inversely proportional to the ratio of the exchange flow rate \( \alpha Q \) between the ideally mixed region, \( V_m \), and stagnant region, \( V_d \), and the flow rate \( Q \) through the system, i.e inversely proportional to \( \alpha \). However, while the dimensionless variance is larger than one, indicating pathological behavior, the central volume principle is satisfied and \( \mu_1 = \tilde{t} \). Hence, regarding stagnancy we can adopt a simple empirical rule. We will get an indication of stagnancy (dead volume) either from the fact that \( \mu_1 < \tilde{t} \), in which case the variance can be anything, or if our data are accurate enough and \( \mu_1 = \tilde{t} \), one can detect stagnancy from \( \sigma_E^2 > 1 \).
You should note that if $\alpha \to \infty$, that is if the exchange flow rate $\alpha Q$ between $V_m$ and $V_d$ is infinitely faster than flow rate through the system itself, $Q$, we recover $\bar{\sigma}_E^2 = 1$ and as evident from the expression for $\bar{E}(s)$ we recover the perfect mixer response. After all infinitely fast (instantaneous) mixing between all regions of the system is the definition of the perfect CSTR, so we should not be surprised by this result.

It should be clear from the above discussion, however, that just from the fact that the dimensionless variance is larger than one we cannot tell whether we deal with stagnancy or bypassing. To be able to distinguish between the two we should examine the shape of the E-curve and especially of the intensity fraction $\Lambda$.

It is tempting to talk about bypassing, if pathology is detected at small times, (e.g. a peak at small times) and of stagnancy, if pathology is present at large times (e.g. a peak at very large times). However, small and large time are ill defined. It may be tempting to say that if the problem is caused by fluid residing less than the characteristic reaction time, $\tau_R$, in the vessel we have a bypassing problem, and if the problem is caused by fluid of residence times order of magnitude larger than $\tau$, then stagnancy is the culprit.

This argument can be summarized as follows:

$$k \frac{C_{ao}}{n - 1} t >> 1 \text{ stagnancy model is justified}$$
$$k \frac{C_{ao}}{n - 1} t << 1 \text{ bypassing model is justified}$$

One can argue that stagnancy is justified if there is a significant fraction of the outflow with the residence times $t$ much larger than characteristic reaction times i.e.

$$\int_{t = \frac{1}{kC_{ao}^{n-1}}}^{\infty} E(t)dt > 0.1$$  \hspace{1cm} (59a)$$

$$1 - F\left(\frac{1}{kC_{ao}^{n-1}}\right) > 0.1$$  \hspace{1cm} (59b)$$

Bypassing is then considered as a model if there is a significant fraction of fluid that emerges at times much less than the characteristic reaction time.
\[ \int_{t=0}^{t} \frac{1}{kC_0} E(t) \, dt > 0.1 \]  
\[ F(t) > 0.1 \]  

However, if one adopts these definitions then even PFR can exhibit bypassing if \( \bar{t} < t_r \), and CSTR can exhibit both bypassing or stagnancy as illustrated below:

\[ E_{CSTR}(t) = \frac{1}{t} e^{-\bar{t}/t} \]  

\[ \int_{t_r}^{\infty} E_{CSTR}(t) \, dt = -e^{-\bar{t}/t} \bigg|_{t_r}^{\infty} = e^{-\bar{t}/t} > 0.1 \]  

which certainly is true whenever

\[ \frac{t_r}{\bar{t}} < \ln 10 \]  

which would then indicate "stagnancy". Similarly, bypassing would be indicated whenever

\[ -e^{-\bar{t}/t} \bigg|_{0}^{t_r} = 1 - e^{-t_r/\bar{t}} > 0.1 \]

\[ 0.9 > e^{-t_r/\bar{t}} \]  

i.e. for all \( \frac{t_r}{\bar{t}} > \ln \left( \frac{1}{0.9} \right) \).

To preclude considering stagnancy and bypassing for a perfect mixer (CSTR), and to reserve stagnancy and bypassing for pathological systems only, we say that only systems that are pathological \( \left( \frac{\sigma^2}{\bar{t}} > 1, \text{ or } \frac{dN}{dt} > 0 \right) \) exhibit either stagnancy or bypassing depending on the criteria above.

---

**Example**

Let us consider again the ill fated mixed reactor of our Example problem that was represented by the Cholette-Cloutier model.

Characteristic reaction time is:

\[ \tau_r = \frac{1}{kC_{A_0}} = \frac{1}{32.8} = 0.03 \text{ min} = 1.8 \text{ s} \]

Characteristic design process time

\[ \bar{t} = \frac{V}{Q} = \frac{25}{1} = 25 \text{ min} \]
Actual characteristic process time

\[ \tau_p = \frac{V_a}{Q_a} = \frac{0.57 \times 25}{0.78 \times 1} = 18.3 \text{ min} \]

An actual ideal CSTR has in the outflow the following fraction of fluid of residence times between 0 and \( \tau_R \)

\[
\int_0^{\tau_R} E_{CSTR}(t) \, dt = \frac{1}{t} \int_0^{\tau_R} e^{-t/t} \, dt = 1 - e^{-\tau_R/t} \\
= 1 - e^{-0.03/25} = 1 - e^{-0.0012} \\
= 1 - 0.9988 = 0.001
\]

Our flow pattern in the above example problem yields an outflow with the fraction of residence times between 0 and \( \tau_R \) of:

\[
\int_0^{\tau_R} E(t) \, dt = \int_0^{\tau_R} (1 - \alpha) \delta(t) \, dt + \int_0^{\tau_R} \frac{\alpha^2}{\beta t} e^{-\alpha t/\beta} \, dt \\
= 1 - \alpha + \alpha \left( 1 - e^{-\alpha \tau_R/\beta t} \right) \\
= 1 - 0.78 + 0.78 \left( 1 - e^{0.78 \times 0.03/0.57 \times 25} \right) \\
= 0.22 + 0.78 \left( 1 - e^{-0.001642} \right) \\
= 0.22 + 0.78 \left( 1 - 0.9984 \right) = 0.22 + 0.001 = 0.221
\]

Since this is much larger than 0.001, and we know that the system is pathological, i.e. \( \sigma^2 > 1 \), it is clear that bypassing contributed significantly to our problem of low conversion.

Now let us examine the effect of stagnancy, which we suspect since \( \mu < \bar{\tau} \)

\[
\int_{\tau_R}^{\infty} E(t) \, dt = \int_{\tau_R}^{\infty} (1 - \alpha) \delta(t) \, dt + \int_{\tau_R}^{\infty} \frac{\alpha^2}{\beta t} e^{-\alpha t/\beta} \, dt \\
= 0 + \alpha e^{-\alpha \tau_R/\beta t} = 0.78 e^{-0.001642} = 0.779
\]

Indeed stagnancy also contributes to the problem.

Ultimately, the best way to check for pathological behavior (e.g. bypassing or stagnancy) is by examination of the intensity function, \( \Lambda(t) \)

Lack of undesirable behavior is indicated by

\[
\frac{d^2 \Lambda}{dt^2} \geq 0 \tag{63}
\]
Fluid passes through the vessel in a regular fashion. The longer the fluid element has been in the vessel (the larger its age) the more probable that it will exit in the next time interval.

Bypassing. Some fluid has increased probability of leaving at a very young age. Rest of the fluid behaves normally.

Stagnancy. After main flow leaves, the probability of the fluid caught in the dead zones to exit decreases until very large ages are reached at which point all fluid must ultimately leave.

Note that the above definition of stagnancy via the \( \Lambda \) function will not detect an entirely 'dead' volume as used initially as our example for a single CSTR with dead volume on page 29. This we can only detect from the fact that the central volume principle is not satisfied \( (\mu_i < \bar{t}) \).

For a CSTR

For a PFR

Additional ways of dealing with stagnancy via the introduction of the holdup function have been discussed by Tester and Robinson in the AIChE Journal in the 1980s.

Example of Determination of System Parameters by Matching Experimentally Determined \( E \) Curve with Model Predicted One via the Method of Moments.

We illustrate here the Method of Moments which we have used above in our examples of CSTR with stagnancy and bypassing.

Recall \( \bar{E}(s) = \int_0^\infty e^{-st} E(t) \, dt \)

Taylor Series Expansion around \( s = 0 \) yields:

\[
\bar{E}(s) = \sum_{n=0}^{\infty} \frac{d^n \bar{E}}{ds^n} (s = 0) \frac{s^n}{n!}
\]
\[
\frac{dE}{ds} \bigg|_{s=o} = E(s = o) = \int_{0}^{\infty} E(t) dt = \mu_o
\]

\[
\frac{dE}{ds} \bigg|_{s=o} = \left(-\int_{0}^{\infty} e^{-st} E(t) dt\right) \bigg|_{s=o} = \int_{0}^{\infty} t E(t) dt = -\mu_1
\]

Hence,

\[
\mu_n = (-1)^n \frac{d^n E}{ds^n} \bigg|_{s=o}
\]

\[
E(s) = \sum_{n=0}^{\infty} (-1)^n \frac{\mu_n}{n!} s^n = \mu_0 - \mu_1 s + \frac{\mu_2}{2} s^2 - \frac{\mu_3}{6} s^3
\]  \hspace{1cm} (A)

\[
E(s) = \sum_{n=0}^{\infty} \frac{d^n E}{ds^n} (0) \frac{s^n}{n!}
\]  \hspace{1cm} (B)

By comparison of (A) and (B) moments can be obtained. For our stirred tank with bypassing and stagnancy example,

\[
E = 1 - \alpha + \frac{\alpha}{1 + \frac{\beta}{\alpha} i s}
\]

\[
E = 1 - \alpha + \alpha \left[1 - \frac{\beta i}{\alpha} s + \frac{\beta^2}{\alpha^2} i^2 s^2 \right]
\]

\[
E = 1 - \alpha + \alpha - \beta i s + \frac{\beta^2}{\alpha} i^2 s^2
\]

\[
E = 1 - \beta i s + \frac{\beta^2}{\alpha} i^2 s^2
\]

\[
\mu_0 = 1 \hspace{1cm} \mu_1 = \beta i
\]

\[
\mu_2 = \frac{2 \beta^2 i^2}{\alpha}
\]

\[
\sigma^2 = \frac{2 \beta^2 i^2}{\alpha} - \beta^2 \frac{i^2}{\alpha} = \frac{\beta^2 i^2}{\alpha} [2 - \alpha]
\]

\[
\sigma^2_D = \frac{\sigma^2}{\mu_1^2} = \frac{\beta^2 i^2 \frac{2-\alpha}{\alpha}}{\beta^2 i^2} = \frac{2-\alpha}{\alpha} = \frac{2-0.78}{0.78} = 1.56
\]

From the tracer experiment we get experimentally

\[
\bar{i}_{exp} = \beta i
\]

\[
\frac{\sigma^2_{i_{exp}}}{\bar{i}_{exp}^2} = \frac{2 - \alpha}{\alpha} = 1.56
\]
Models for Nonideal Reactors

Approach to Model Development and Parameter Estimation

Two tasks arise:
1. Formulation of a proper configurational model based on: the observed RTD, physical description of the reactor, and partial knowledge of the presumed flow pattern.
2. Evaluation of model parameters by matching the model predicted RTD to the experimental RTD.

Then the model can be used to predict reactor performance at given operating conditions. Use of the model at different conditions requires the knowledge of how the model parameters change with the change in operating parameters.

Matching experimentally determined RTDs to model predicted ones is just one of the many problems that arise in the area of parameter estimation. Parameter estimation is then in general based on minimization of some error criterion, where the error is defined as the difference between the actual and the model predicted value.

The most general error criterion for a system whose response, or certain property, was continuously measured as $y(t)$ and the model predicted response, or property, $h(t, \underline{x}(t,k))$, where $x(t,k)$ are the n-state variables of the system while $k$ is the vector of p-unknown parameters, can be stated as:

$$S = \int_o^\infty G[y(t) - h(t, \underline{x}(t,k))]Q(t)dt$$

or if data is available at only R discrete points in time:

$$S = \sum_{i=1}^{R} G[y(t_i) - h(t_i, \underline{x}(t_i,k))]Q_i$$

$Q(t)$ is the appropriate weighting function.
The best estimate of parameters is now the choice of parameter vector \( \kappa \) that minimizes the error criterion, \( S \), in same sense.

In RTD theory and practice most often \( y(t) = E_{\text{measured}}(t), \ h(t,\kappa) = E_{\text{predicted}}(t,k) \)

**Parameter Estimation Methods**

Most often used methods for parameter estimation are:

1. **Matching of moments**

   \[
   S = \int_o^\infty [E_m(t) - E_p(t,k)]t^n \, dt, \quad n = 0,1,2... \tag{1}
   \]

2. **Unweighted least squares in time domain**

   \[
   \min_{k} S = \min_{k} \int_o^\infty [E_m(t) - E_p(t,k)]^2 \, dt \tag{2}
   \]

3. **Frequency response least squares (matching of transfer function and transformed data for \( s = i\omega \))**

   \[
   \min_{k} S = \int_o^\infty \left\{ \left( \text{Re} \ E_m(\omega) - \text{Re} \ E_p(\omega,k) \right)^2 + \left( \text{Im} \ E_m(\omega) - \text{Im} \ E_p(\omega,k) \right)^2 \right\} d\omega \tag{3}
   \]

4. **Integral absolute error in the transform domain**

   \[
   \min_{k} S = \int_o^\infty |E_m(s) - E_p(s,k)| \, ds \tag{4}
   \]

5. **Integral square error in the transform domain**

   \[
   \min_{k} S = \int_o^\infty \left[ |E_m(s) - E_p(s,k)|^2 \right] \, ds \tag{5}
   \]

6. **Weighted moments method**

   \[
   \min_{k} S = \int_o^\infty \left[ E_m(t) - E_p(t,k)^t \right] e^{-at} - e^{-by} \, dt \tag{6}
   \]

The method of moments places too much weight and over-emphasizes too much the tail of the curve which is usually inaccurately measured. It is popular due to simplicity.
Least squares method in time domain is the equivalent of the least squares in frequency domain due to Parseval’s theorem.

\[
\int_{-\infty}^{\infty} \tilde{F}^2(t)dt = \frac{1}{2\mu} \int_{-\infty}^{\infty} \left| \tilde{F}(\omega) \right|^2 \tag{7a}
\]

\[
\tilde{F}(\omega) = F(t) = \int_{-\infty}^{\infty} F(t) e^{-\text{tot}} dt = \text{Re} \tilde{F}(\omega) + i / m \tilde{F}(\omega) \tag{7b}
\]

Least squares in transform domain weight heavily the errors at small times. Integral absolute errors in transform domain corresponds to least squares in time domain with

\[
Q(t) = \frac{e^{-s \cdot t} - e^{-s \cdot t}}{t}
\]

Other Important Relations

Noncentral moments are defined as

\[
\mu_n = \int_0^{t^n} E(t)dt = (-1)^n \frac{d^n E}{ds^n} \bigg|_{s=0} \tag{8}
\]

Central moments are defined as

\[
\mu_n = \int_0^t (t - \mu)^n E(t)dt \tag{9}
\]

\[
\bar{E}(s) = \int_0^t e^{-st} E(t)dt \text{- moment generating function (transfer function)}
\]

\[
\bar{E}_w(s) = \int_0^t e^{-(t-\mu)s} E(t)dt = L \{ E(t-\mu) \} = e^{-\mu s} \bar{E}(s)
\]

\[
= -s \mu + \frac{s^2}{2} \mu_2 + \frac{s^3}{3} \mu_3
\]

\[
\mu_n = (-1)^n \frac{d^n}{ds^n} [e^{ns} \bar{E}(s)]
\]
ChE 512: Addendum 2 to Chapter 2

**Evaluation of Flow Model Parameters**

**Task 1** Perform a well controlled tracer study for the system of interest

**Task 2** Eliminate “end” effects

**Task 3** Suggest a flow model for the system

**Task 4** Evaluate model parameters from tracer data

**Task 5** Evaluate model suitability and either change the model or use it

**Task 1)** Proper flow tagging and mixing cup concentration monitoring is essential.

(More about this later when discussing laminar flow)

**Task 2)** Every tracer measurement also includes the response of auxiliary lines in front and after the equipment of interest and of the measuring device itself. Deconvolute “the system” response from the “auxiliary system response” as per the sketch below:

```
\[ G_I(t) \quad E \quad G_S(t) \quad E_m(t) \]
```

The normalized impulse tracer response at the exit \( E_m(t) = Q \frac{C_m(t)}{m_T} \) is obtained from the measured impulse tracer response at the exit \( C_m(t) \) divided by the ratio of the tracer mass, \( m_T \), that was instantaneously injected at the inlet and the steady flow rate, \( Q \). This measured impulse response represents the convolution of the injection system, \( G_I(t) \), our system of interest, \( E(t) \), and sampling system \( G_S(t) \). In the Laplace domain this is:

\[
E_m(s) = \overline{G_I(s)} \overline{E(s)} \overline{G_J(s)} = \overline{E(s)} \cdot \overline{G_n(s)}
\]

where \( \overline{G_n(s)} = \overline{G_I(s)} \cdot \overline{G_J(s)} \) is the transfer function for the auxiliary system.

The above eq (1) is only true if we have taken precautions to satisfy the conditions of the proper tracer test, (i.e. with respect to tracer injection and choice of tracer, if we have a monitoring, closed system, etc.) and if we have demonstrated invariance of \( E_m(t) \) to the mass of tracer injected, i.e. \( C_m \) doubles as \( m_T \) doubles!
Assuming that the above conditions are satisfied, we perform deconvolution of eq (1) to extract \( E(t) \) which is of interest to us

\[
\overline{E}(s) = \frac{E_m(s)}{G_a(s)} \tag{2}
\]

\[
E(t) = L^{-1}\{\overline{E}(s)\} \tag{3}
\]

In order to perform the operations required by eq (1) we need to know \( G_a(s) \). This knowledge can be obtained in several ways:

a) - by removing the system of interest out of the experimental configuration and obtaining a unit impulse tracer response (i.e. transfer function) for the auxiliary system itself

b) - by using a model for \( G_a(s) \) and attempting to quantify the model by independent experiments.

The most popular models are:

i) – simple time lag \( G_a = e^{-t_2s} \)

ii) – first order process \( G_a = \frac{1}{1 + \frac{t_a}{s}} \)

iii) – combination of first order and time lag \( \frac{e^{-t_{a1}s}}{1 + \frac{t_{a2}}{s}} \)

iv) – second order response plus time lag, etc.

v) – actual physical model

The less spreading of the response occurs in the auxiliary system, the more justified the use of simple time lag \( e^{-t_2s} \) where \( t_2 = \frac{V_a}{Q} + \tilde{t}_{\text{instrument}} \)

This is OK for many plant data. In laboratory or pilot work often an exact \( G_a \) is needed.

**Note:** From \( E(t) \) data that is experimentally obtained we can get \( \overline{E}(s) = \int_0^s e^{-st}E(t)dt \) by using a number of routine numerical programs. No difficulty involved in this step. In the same
way from the experimentally determined $G(t)$ we can get $\mathcal{G}(s) = \int_0^\infty e^{-st}G(t)dt$. However, performing eq (2) is non-trivial due to the inherent noise of the routine deconvolution package programs. (Routinely $s = i\omega$ is used and Fourier transform is utilized to perform the inversion). This step can create a completely distorted $E(s)$. Thus, filtering algorithms must be used (see Mills and Dudukovic, AIChE J 34(10), 1752 (1988)).

Inversion back to time domain by eq (3) can also be tricky

$$E(t) = \frac{1}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} e^{st} \mathcal{E}(s)dt$$

(4)

If all of the above is done correctly then we have the experimentally determined $E(t) = E_e(t)$ that we can try to match to model predicted one $E_p(t)$.

An alternative, which allows us to avoid deconvolution, is to convolute the measured $G_a(t)$ with model predicted $E_p(t)$ to generate the predicted $E_{mp}(t)$ which can be matched to experimental observations directly. This approach is to be preferred.

**Task 3)** In this step we suggest a model that is simple but seems to be able to capture the essence of experimental observations. This model then has a predicted impulse response $E_p(t, P)$ where $P$ is the vector of the parameters of the model.

**Task 4)** Our task now is to match $E_p(t, P)$ with $E_e(t)$ [or $E_{mp}(t, P)$ to $E_m(t)$].

In general then we will have a difference at each sampling time $t_i$ between measured value $E_p(t_i)$ and predicted values $E_p(t_i)$. We want to minimize some function $g$ of that difference, $g[E_e(t_i) - E_p(t_i, P)]$ weighted with appropriate weights $Q_i$ over all times by selecting $P$ in the best possible way.

The problem can be stated as

$$\min_P \mathcal{S} = \min_P \sum_{i=1}^N g[E_e(t_i) - E_e(t_i, P)]Q_i$$
Our result for the parameters that provide “best match” depends on the choice of \( g \) and \( Q \).

The most frequently used methods are:

A) The Method of Moments

\[
Q(t) = t^n; \quad g = E_e(t) - E_p(t, P)
\]

\[
\int_\alpha^\infty [E_e(t) - E_p(t, P)]t^n dt = O \text{ for } 0,1,2,...N
\]

where \( N \) is the dimensionality of the vector \( P \)

\[
\int_\alpha^\infty E_e(t)t^n dt = \mu_n(P)
\]

(values from exp data) – (moments of the system as function of system parameter)

This is a favored method due to simplicity but requires accurate data and tends to be inaccurate for moments larger than the second moment.

b) Weighted moments

\[
Q(t) = t^n \left[e^{-at} - e^{-bt}\right] \quad g = E_e(t) - E_p(t, P)
\]

\[
\int_\alpha^\infty [E_e(t) - E_p(t, P)]t^n \left[e^{-at} - e^{-bt}\right] dt = 0
\]

Tail effects are de-emphasized. Guidance for selection of \( a \) and \( b \) is provided. Analytical solution possible.

c) Least squares in time domain

\[
Q = 1 \quad g = (E_e - E_p)^2
\]

\[
\min_\varepsilon \int_\alpha^\infty [E_e(t) - E_p(t, P)]^2 dt
\]

Run a nonlinear parameter estimation package
\[
\int_0^\infty \left[ E_e(t) - E(t,P) \right] \frac{\partial E_p}{\partial p_i} dt = 0 \quad \text{for } i = 1, 3 \ldots N
\]

In general N nonlinear eqs to solve for the N p_i s!

In the above \( Q \neq 1 \) can be introduced.

D) Least squares in frequency domain

\[
Q = 1 \quad g = \overline{E_e}(\omega) - \overline{E_p}(\omega, P^2)
\]

\[
\min_p \left\{ \frac{1}{2\pi} \int_0^{\infty} \left[ \text{Re} \ \overline{E_e}(\omega) - \text{Re} \ \overline{E_p}(\omega, P) \right]^2 + \left[ \text{Im} \ \overline{E_e}(\omega) - \text{Im} \overline{E_p}(\omega, P) \right]^2 \right\} dt
\]

Really the same as least squares in time domain due to Parseval’s theorem

\[
\int_{-\infty}^{\infty} F^2(t) dt = \frac{1}{2\pi} \int_{-\infty}^{\infty} |F(\omega)|^2 d\omega
\]

\[
\overline{F}(\omega) = F \left[ F(t) \right] = \int_{-\infty}^{\infty} F(t)e^{-i\omega t} dt = \text{Re} \ F(\omega) + i \ \text{Im} \ F(\omega)
\]

E) Integral absolute error in transform domain

\[
\text{Min}_p \ S \quad S = \int_0^{\infty} \left\{ \left| E_e(s) - E_p(s, P) \right| \right\} ds
\]

This corresponds to least squares in time domain with \( \overline{E} = L(E(t)) \)

\[
Q(t) = \frac{e^{-st} - e^{-syt}}{t}
\]

F) Integral square error in transform domain

\[
\min_p \ S \quad S = \int_0^{\infty} \left\{ \left| E_e(s) - E_p(s, P) \right| \right\}^2 ds
\]

emphasizes errors at small times.

**Note:** One should keep in mind that in most practical situations the above general techniques will be bypassed. By selecting simple models often model testing can be done in a simpler way. For example

- semilog plots will reveal CSTR behavior or two CSTRs with distinctly different \( \bar{t}, s \)
- from the peak, width or height of the curve model parameters can be evaluated for N CSTRs
\[ Q_{\text{max}} = \frac{N - 1}{N} \]
\[ \frac{\Delta \theta}{\theta_{\text{max}}} = \frac{2}{\sqrt{N-1}} \quad \text{at } E_{\text{inf}} \text{ etc} \]

When using the method of moments it is the easiest to evaluate the moments of the model from its Laplace transform

\[ \mu_n = \int_0^\infty t^n E(t) dt \]
\[ \bar{E} = \int_0^\infty e^{-st} E(t) dt \]
\[ \frac{d\bar{E}}{ds} = -\int_0^\infty e^{-st} tE(t) dt \]
\[ \frac{d^n \bar{E}}{ds^n} = (-1)^n \int_0^\infty e^{-st} t^n E(t) dt \]
\[ \left. \frac{d^n \bar{E}}{ds^n} \right|_{s=0} = (-1)^n \int_0^\infty t^n E(t) dt = (-1)^n \mu_n \]

Thus \[ \mu_n = (-1)^n \left. \frac{d^n \bar{E}}{ds^n} \right|_{s=0} \]

Often it is much easier to expand \( \bar{E}(s) \) by Taylor theorem around \( s = 0 \) and identify the moments from such an expansion

\[ \bar{E}(s) = \sum_{n=0}^\infty \frac{d^n \bar{E}}{ds^n} \bigg|_{s=0} s^n/n! = \sum_{n=0}^\infty (-1)^n \frac{\mu_n}{n!} s^n \]
\[ = \mu_0 - \mu_1 s + \frac{\mu_2}{2!} s^2 - \frac{\mu_3}{3!} s^3 \]

Example: Find \( \mu_0, \mu_1, \mu_2, \sigma^2 \) for \( N \)-CSTRs in series:

\[ \bar{E}_N(s) = \frac{1}{\left(1 + \frac{\bar{t}}{N} s\right)^N} \]

Bimodal theorem

\[ (1 + x)^\alpha = 1 + \alpha x + \frac{\alpha(\alpha - 1)}{2!} x^2 + \frac{\alpha(\alpha - 1)(\alpha - 2)}{3!} x^3 \]
\[ \alpha = -N \quad x = \frac{\bar{t}}{N} s \]
\[ \bar{E}_N(s) = 1 - N \frac{\bar{t}}{N} s + \frac{-N(-N-1)}{2!} \left( \frac{\bar{t}}{N} s \right)^2 \]

\[ \bar{E}_N(s) = 1 - \bar{t} s + \frac{(n + 1) \bar{t}^2}{N2!} + 0(s^2) \]

\[ \bar{E}(s) = \mu_0 - \mu_t s + \frac{\mu_2}{2!} s^2 + 0(s^2) \]

By comparison
\[
\begin{align*}
\mu_0 &= 1 \\
\mu_t &= \bar{t} \\
\mu_2 &= \frac{N + 1}{N} \bar{t}^2
\end{align*}
\]

\[ \sigma^2 = \mu_2 - \mu_t^2 = \frac{N + 1}{N} \bar{t}^2 - \bar{t}^2 = \frac{N + 1 - N}{N} \bar{t}^2 = \frac{1}{N} \bar{t}^2 \]

\[ \overline{\sigma^2} = \frac{\sigma^2}{\mu_2} = \frac{\bar{t}^2}{N \bar{t}^2} = \frac{1}{N} \]

**Task 5** Plot model prediction vs data, evaluate mean absolute and relative error, judge by requirements on the model whether the fit is suitable.

For an Introduction to parameter estimation of reactor models from tracer data see:

Let us assume for the moment that we can calculate from the knowledge of the flow pattern the RTD of the system or that we can readily obtain it experimentally on a reactor prototype. Is the reactor performance uniquely determined by its RTD? This seems to be a pertinent question to ask.

We already know that every flow pattern has a unique RTD. Unfortunately a given RTD does not determine the flow pattern uniquely. Two examples to illustrate this are shown below.

**EXAMPLE 1:**

![Diagram of two systems with the same RTD](image.png)

**FIGURE 1:** Schematic of two systems with the same RTD.

The E function for both system 1a and 1b is:

\[
E(t) = \frac{2}{t} e^{-\frac{3(t-\frac{7}{2})}{t}} H(t - \frac{7}{2}); \quad \bar{E}(s) = \frac{e^{-\frac{s}{2}}}{1 + \frac{s}{2}}
\]

where \( H(t - a) = \begin{cases} 0 & t < a \\ 1 & t > a \end{cases} \) is the Heaviside's unit step function.
FIGURE 2: Impulse response of both systems 1a and 1b.

EXAMPLE 2:

2a.

2b.

FIGURE 3: Schematic of two flow systems with the exponential E curve.
The E-curve for both systems 2a and 2b is:

\[ E(t) = \frac{1}{t} e^{-t/t} \]

\[ E(s) = \frac{1}{1 + ts} \]

**FIGURE 4:** Impulse response for systems 2a) and 2b).

If the RTD of the reactor determines its performance uniquely, then systems 1a and 1b should yield the same conversion for all reaction orders. Systems 2a and 2b should also behave alike. We suspect that this will not be the case because we recall that reaction orders higher than one will give higher conversions if mixing is delayed, and hence we suspect that system 1a will perform better than 1b and system 2b better than 2a. For a first order process conversion is entirely determined by the residence time of the individual reactant elements in the reactor, not by their surroundings in the reactor, and hence we suspect that systems 1a and 1b will perform the same, and systems 2a and 2b will perform alike. For reaction orders less than one we suspect that the behavior will be the opposite to that for orders larger than one.

Let us consider first a 1st order irreversible reaction at constant temperature and of constant density in systems 1a and 1b.
SYSTEM 1a:

First reactor PFR: \[
\frac{\dot{\ell}}{2} = \int_{c_A}^{c_{A0}} \frac{dC_A}{kC_A} = \frac{1}{k} \ell n \frac{C_{A0}}{C_A1}
\]

Second reactor CSTR: \[
\frac{\dot{\ell}}{2} = \frac{C_{A1} - C_{A2}}{kC_{A2}}
\]

Hence, \[1 - x_{A2} = \frac{C_{A2}}{C_{A0}} = \frac{e^{-\frac{kt}{2}}}{1 + \frac{kt}{2}}\]

SYSTEM 1b:

First reactor CSTR: \[
\frac{\dot{\ell}}{2} = \frac{C_{A0} - C_{A1}}{kC_{A1}}
\]

Second reactor PFR: \[
\frac{\dot{\ell}}{2} = \int_{c_A}^{c_{A1}} \frac{dC_A}{kC_A} = \frac{1}{k} \ell n \frac{C_{A1}}{C_{A2}}
\]

\[1 - x_{A2} = \frac{C_{A2}}{C_{A0}} = \frac{e^{-\frac{kt}{2}}}{1 + \frac{kt}{2}}\]

\[x_{A2} = x_{A2}' = 1 - \frac{e^{-Da/2}}{1 + Da/2}\] where \(Da = Da_i = k\tilde{t}\)

Just as we expected the performance of the system is entirely determined by its RTD for a first order reaction. This can readily be generalized to an arbitrary network of first order processes.

Now consider a 2nd order irreversible reaction taking place in system 1.

SYSTEM 1a:

First reactor PFR: \[
\frac{\dot{\ell}}{2} = \int_{c_A}^{c_{A0}} \frac{dC_A}{kC_A} = \frac{1}{k} \ell n \frac{C_{A1}}{C_{A0}} - \frac{1}{C_{A0}}
\]
Second reactor CSTR: \[
\frac{\dot{t}}{2} = \frac{C_{A1} - C_{A2}}{kC_{A2}^2}
\]

\[
1 - x_{A2} = \frac{C_{A2}}{Ca_o} = \sqrt{1 + \frac{2ktCAo}{1 + k \frac{\dot{t}}{2} CAo}} - 1
\]

**SYSTEM 1b:**

First reactor CSTR: \[
\frac{\dot{t}}{2} = \frac{CAo - C_{AI1}}{kCAI1^2}
\]

Second reactor PFR: \[
\frac{\dot{t}}{2} = \frac{1}{k} \left( \frac{1}{CA2} - \frac{1}{C_{AI1}} \right)
\]

\[
1 - x_{A2} = \frac{C_{A2}'}{Ca_o} = \frac{\sqrt{1 + 2ktCAo} - 1}{\frac{kt}{2} \left[ 2 + \sqrt{1 + 2ktCA_0} - 1 \right]}
\]

Note that both expressions for conversion are a function of the Damkohler number for the system, where \( Da = Da_2 = k\dot{t} CA_o \).

\[
x_{A2} = 1 - \frac{1}{Da} \left[ \sqrt{1 + \frac{2Da}{1 + Da/2}} - 1 \right]
\]

\[
x_{A2}' = 1 - \frac{2}{Da} \left[ \sqrt{1 + 2Da} - 1 \right] \]

The table below compares the results for various values of the Damkohler number.

<table>
<thead>
<tr>
<th>( Da )</th>
<th>( x_{A2} )</th>
<th>( x_{A2}' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.472</td>
<td>0.464</td>
</tr>
<tr>
<td>2</td>
<td>0.634</td>
<td>0.618</td>
</tr>
<tr>
<td>4</td>
<td>0.771</td>
<td>0.750</td>
</tr>
</tbody>
</table>

You should plot now \( x_{A2} \) and \( x_{A2}' \) vs \( Da \). You will find that \( x_{A2} > x_{A2}' \). When is this difference larger, at low or high values of \( Da \)?
For a reaction of half order \((n = 1/2)\) we get

\[
\frac{x_{A_2}}{2} = \frac{Da}{2} - 3\frac{Da}{16} + \frac{Da}{2} \sqrt{1 - \frac{Da}{2} + \frac{Da^2}{8}}
\]

for system 1a

\[
x_{A_2}' = Da \sqrt{1 + \frac{Da^2}{16}} - 5\frac{Da}{16}
\]

for system 1b

\[
\begin{array}{ccc}
\text{Da} & x_{A_2} & x_{A_2}' \\
0.5 & 0.424 & 0.426 \\
1 & 0.708 & 0.718 \\
2 & 0.957 & 0.986 \\
\end{array}
\]

You should check the above expressions and draw your own conclusions by plotting \(x_{A_2}\) and \(x_{A_2}'\) vs \(Da = Da_{1/2} = \frac{k_\tau}{C_{Ao}^{1/2}}\).

Let us now consider system 2 and a lst order irreversible reaction.

**SYSTEM 2a:**

\[
x_{A_a} = \frac{Da}{1 + Da}
\]

**SYSTEM 2b:**

\[
C_{A_i} = \frac{C_{A_o}}{1 + \alpha k_\tau}
\]

is the exit reactant concentration from the 1st CSTR.

\[
C_{A_2} = \frac{C_{A_i}}{1 + k_\tau} = \frac{C_{A_o}}{(1 + k_\tau)(1 + \alpha k_\tau)}
\]

is the exit reactant concentration from the 2nd CSTR.
The balance around the mixing point where the two streams join yields:

\[
C_{A_1} = \alpha C_{A_1} + (1 - \alpha) C_{A_2} = C_{A_0} \left[ \frac{\alpha}{1 + \alpha k\tau} + \frac{1 - \alpha}{(1 + k\tau)(1 + \alpha k\tau)} \right] =
\]

\[
\frac{C_{A_0} \left( \alpha + \alpha k\tau + 1 - \alpha \right)}{(1 + \alpha k\tau)(1 + k\tau)} = \frac{C_{A_0}}{1 + k\tau} = \frac{C_{A_0}}{1 + Da}
\]

Hence,

\[
x_{A_2} = 1 - \frac{C_{Ab}}{C_{A_0}} = \frac{Da}{1 + Da}
\]

\[
x_{A_2} = x_{A_0}
\]

For an exercise consider System 2 and a 2nd order reaction and then a zeroth order reaction. Are the conversions now different? Why?
3.1 SEGREGATED FLOW MODEL

The above examples demonstrate that the RTD of the reactor determines its performance uniquely in case of first order processes. In a first order process conversion is determined by the time spent by individual fluid reactant elements in the reactor, not by their environment in the reactor. Let us generalize this conceptually in the following way. Assume that all the elements of the inflow can be packaged into little parcels separated by invisible membranes of no volume. Mixing among various parcels is not permitted, i.e., no elements can cross the membranes (parcel walls) except at the very reactor exit where the membranes vanish and the fluid is mixed instantaneously on molecular level. Consider the life expectation density function of the inflow $L_i$ and define it as

$$L_i(t) \, dt = \text{(fraction of the elements of the inflow with life expectancy between }\ t \ \& \ t + dt\text{)}$$

(54)

Clearly, due to steady state, if we look at the inflow at time $t = 0$ and if we could substitute among white fluid a parcel of red fluid for the elements of the inflow of life expectancy, $t_i$, then $t_i$ seconds later the red parcel would appear at the outlet and would represent the elements of the outflow of residence time $t_i$. Hence, at steady state the life expectation density function for the inflow equals the exit age density function

$$L_i(t) = E(t)$$

(55)

Hopefully, it is clear to everyone that since the flow rate is constant, and there can be no accumulation, the fraction of the fluid entering with life expectancy of $t_i$ must equal the fraction of the fluid exiting with residence time $t_i$. This means that we can consider that each of our hypothetical parcels formed at the inlet engulfs the fluid of the same life expectancy. When parcels reach the exit, each parcel will contain fluid of the same residence time specific to that parcel. Since, there is no exchange between parcels during their stay in the reactor, each can be considered a batch reactor. The reactant concentration at the outflow is then obtained by mixing all the parcels of all residence times in the right proportion dictated by the exit age density function and can be expressed as:

$$C_{A_{out}} = \sum_{dtt_i} \left( \text{reactant concentration after batch reaction time } t_i \right) \times \left( \text{fraction of the outflow of residence time around } t_i \right)$$
\[ C_{\text{out}} = \lim_{N \to \infty} \sum_{i=1}^{N} C_{\text{batch}}(t_i) \Delta t_i \]
\[ \Delta t_i \to 0 \]
\[ N \to \infty \]

\[ C_{\text{out}} = \int_{0}^{\infty} C_{\text{batch}}(\tau) E(\tau) \, d\tau \]  \hspace{1cm} (56)

where \( C_{\text{batch}} \) is obtained from the reactant mass balance on a batch reactor, which for an n-th order reaction takes the following form:

\[ -\frac{dC_{\text{batch}}}{d\tau} = kC_{\text{batch}}^n; \text{ at } \tau = 0; \quad C_{\text{batch}}(0) = C_{A0} \]  \hspace{1cm} (57)

Now for a 1st order irreversible reaction:

\[ C_{\text{batch}}(\tau) = C_{A0} e^{-k\tau} \]  \hspace{1cm} (58)

so that

\[ C_{\text{out}} = C_{A0} \int_{0}^{\infty} e^{-k\tau} E(\tau) \, d\tau \]  \hspace{1cm} (56a)

The above expression is nothing else but the Laplace transform of the \( E \) function evaluated at \( s = k \), i.e., Laplace transform variable takes the numerical value of the rate constant.

Conversion can then be calculated as:

\[ x_A = 1 - \frac{C_{\text{out}}}{C_{A0}} = 1 - \int_{0}^{\infty} e^{-k\tau} E(\tau) \, d\tau = 1 - \left. E(s) \right|_{s=k} \]  \hspace{1cm} (56b)

Using the above formula we get:

**For system 1:**

\[ x_A = 1 - \frac{e^{-k\frac{t}{2}}}{1 + k\bar{t} / 2} = 1 - \frac{e^{-Da\bar{t}/2}}{1 + Da / 2} \]  \hspace{1cm} (59a)

**For system 2:**

\[ x_A = 1 - \frac{1}{1 + k\bar{t}} = \frac{k\bar{t}}{1 + k\bar{t}} = \frac{Da}{1 + Da} \]  \hspace{1cm} (59b)

In terms of dimensionless quantities, \( \bar{t} E(t) = E_{\theta}(\theta) \), and for a first order reaction we can write:
The model that we have just developed is called the segregated flow model because it assumes that the fluid elements that enter together always stay together and are surrounded at all times by the fluid elements of the same age, except at the outlet where they finally mix intimately with elements of all ages in proportion dictated by the residence time density function \( E(t) \). A fluid for which this model is applicable behaves as a macro fluid and has the tendency of travelling in clumps. As we have seen the segregated flow model gives the exact prediction of performance for 1st order reactions, but formula (56) is general and predicts exit concentration for any reaction order for a macro fluid. However, for nonlinear rate forms, \( n \neq 1 \), as we have seen from our examples, reactor performance does not only depend on the RTD but also on the details of the mixing pattern. Hence, formula (56) cannot predict for \( n \neq 1 \) the exact performance but perhaps predicts a bound on the performance. In dimensionless form, the prediction of the segregated flow model is:

\[
x_A = 1 - \int_0^\infty e^{-Da \theta} E(\theta) \, d\theta = 1 - \frac{E_0(s)\big|_{s = -Da}}{s - Da}
\]  

(56c)

Where for \( n \)-th order irreversible kinetics

\[
\frac{dX_{\text{batch}}^n}{d\theta} = Da \left(1 - x_A\right)^n; \quad \theta = 0, x_A = 0
\]  

(61)

For an \( n \)-th order reaction eq. (60) gives either the upper or lower bound on conversion depending on the concavity (convexity) of the \( x_A \) vs \( \theta \) curve. We always expect to obtain higher conversion in a system where the reaction rate on the average is higher. Eq. (60) requires that mixing between fluid elements of various ages occurs only at the exit. Let us consider only two fluid elements of equal volume but different age, and hence different reactant concentration, and let us examine how mixing or lack of it affects the reaction rate for the system comprised of these two elements. We consider the rate obtainable if the elements are first intimately mixed, \( r_m \), and the rate if they remain unmixed, \( r_{av} \). These two rates are:

\[
r_m = r\left(\frac{C_{A_1} + C_{A_2}}{2}\right) \quad r_{av} = \frac{r(C_{A_1}) + r(C_{A_2})}{2}
\]  

(62)
Rate vs reactant concentration is plotted for reaction orders of $n = 1$, $n > 1$, $n < 1$ in Figure 5. The two fluid elements have concentrations $C_{A1}$, $C_{A2}$, respectively, and the corresponding rates are $r(C_{A1}) = r_1$, $r(C_{A2}) = r_2$. If the fluid elements do not mix, but react each at its own rate, the average rate lies on the chord connecting the points $(C_{A}, r_1)$ and $(C_{A}, r_2)$ and is $r_{av} = \frac{r_1 + r_2}{2}$. If the two fluid elements are mixed first, the concentration in the mixed element of double volume is $C_{Am} = \frac{1}{2} (C_{A1} + C_{A2})$, the rate at this new concentration is $r_{m} = r(C_{Am})$ and lies at the rate vs concentration curve evaluated at the abcissa of $C_{Am}$. Clearly then, whenever the chord lies above the curve (the curve is concave up) $r_{av} > r_{m}$ and late mixing, or fluid segregation by age, leads to increased rate and larger conversion. When the chord is always below the curve $r_{av} < r_{m}$, then late mixing or fluid segregation leads to reduced rates and reduced conversion. For first order reactions micromixing, i.e. earliness or lateness of mixing plays no role, it is only the RTD of the system that counts.

The above discussion can be generalized (see E.B. Nauman and B.A. Buffham, Mixing in Continuous Flow Systems, Wiley, 1983) and a proof can be given that for all monotonic rate forms for which $\frac{d^2r}{dC_A^2} > 0$ the segregated flow model gives the upper bound on conversion, while for the monotonic rate forms for which $\frac{d^2r}{dC_A^2} < 0$ the segregated flow
model gives the lower bound on conversion. For first order processes $\frac{d^2r}{dC_A^2} = 0$ and the segregated flow model gives the exact prediction.

In terms of our examples, the segregated flow model prediction for a 2nd order reaction for Scheme 1 is:

$$x_A = \int_{x_{A_{batch}}}^{\infty} x_{A_{batch}}(\theta) \, 2e^{-\left(\theta - \frac{1}{2}\right)} \, H\left(\theta - \frac{1}{2}\right) \, d\theta$$  \hspace{1cm} (63)

$$\frac{dx_{A_{batch}}}{d\theta} = Da \left(1 - x_{A_{batch}}\right)^2$$  \hspace{1cm} (64)

So that upon integration we get

$$x_{A_{batch}} = \frac{Da\theta}{1 + Da\theta}$$  \hspace{1cm} (65)

Substituting this into the above equation (63) yields:

$$x_A = 2e \, Da \int_{\frac{1}{2}}^{\infty} \frac{\theta e^{-\theta}}{1 + Da\theta} \, d\theta = 2e \left[ \int_{\frac{1}{2}}^{\infty} e^{-\theta} \, d\theta - \int_{\frac{1}{2}}^{\infty} \frac{e^{-\theta}}{1 + Da\theta} \, d\theta \right]$$  \hspace{1cm} (66)

Upon substitution in the second integral of

$$x = \frac{2}{Da} \left(1 + Da\theta\right)$$  \hspace{1cm} (67)
we get
\[ x_A = 1 - \frac{2}{Da} e^{\left(1 + \frac{2}{Da}\right)} \int_1^{\infty} \frac{e^{-x}}{x} \, dx \] (68)

Again it is instructive to plot \( x_A \) for segregated flow vs \( Da \) and compare it to the two models based on ideal reactor concepts for system 1a and 1b. You can find the values of the above integral tabulated as values of one of the family of exponential integrals.

The segregated flow model represents a useful limiting behavior of the system and gives a bound on performance for monotonic rate forms. It's requirements are: i) that the fluid be segregated by age, and ii) that mixing between elements of various ages occurs at the latest possible time, i.e. only at the reactor exit. Thus, every point in the system has its own age i.e. the point age density function in the system is a delta function \( I_p(\alpha) = \delta(\alpha - \alpha_p) \) where \( \alpha_p \) is the mean age for the point under consideration.

Consider the sketch below as a representation of the segregated flow model:

![FIGURE 6a: Schematic of the Segregated Flow Model for All the Fluid.](image)

An element of volume of the system occupied by fluid elements of age between \( \alpha \) and \( d\alpha \) is \( dV = VI(\alpha)d\alpha \). Thus, the volume scale, \( V \), where volume is measured from the reactor entrance, and the age scale are proportional and point in the same direction.

We want now to make a balance on all fluid elements of age between \( \alpha \) and \( \alpha + \Delta\alpha \), i.e. in the differential volume, \( dV = VI(\alpha)d\alpha \) as sketched in the figure.
We can write:

\[
(\text{Elements in the reactor of age about } \alpha + \Delta \alpha) = \\
(\text{Elements in the reactor of age about } \alpha) - \\
(\text{Elements of the outflow of age about } \tilde{\alpha} \text{ collected during time interval } \Delta \alpha)
\]

where \( \alpha \leq \tilde{\alpha} \leq \alpha + \Delta \alpha \). Now with the help of age density functions the above can be written as

\[
VI(\alpha + \Delta \alpha) \Delta \alpha = VI(\alpha) \Delta \alpha - \int_{\alpha}^{\alpha + \Delta \alpha} Q \left[ \int_{\alpha}^{\tilde{\alpha}} E(\alpha) \, d\alpha \right] \, d\alpha 
\]  

(69)

Using the mean value theorem we get:

\[
VI(\alpha + \Delta \alpha) \Delta \alpha - VI(\alpha) \Delta \alpha = -Q \Delta \alpha E(\tilde{\alpha}) \Delta \alpha
\]

Taking the limit as \( \Delta \alpha \to 0 \) yields

\[
\frac{V}{Q} \lim_{\Delta \alpha \to 0} \frac{I(\alpha + \Delta \alpha) - I(\alpha)}{\Delta \alpha} = -\lim_{\Delta \alpha \to 0} E(\tilde{\alpha})
\]  

(69)

\[
\tilde{\gamma} \frac{dI}{d\alpha} = -E(\alpha)
\]

\[
\alpha = \infty \quad I = 0
\]  

(70a)

We have derived, based on the above, the already well known relationship between the I and E function.

Now, based on the above model framework, we focus on the reactant A (see Figure 6B). We make a balance on the fluid elements of reactant between age \( \alpha \) and \( \alpha + \Delta \alpha \).

**FIGURE 6b:** Schematic of the Segregated Flow Model for Reactant A.
(Reactant elements in the reactor of age about $\alpha + \Delta \alpha$) =

(Reactant elements in the reactor of age about $\alpha$) -

(Reactant elements in the outflow of age about $\tilde{\alpha}$ collected during $\Delta \alpha$) -

(Reactant elements in the reactor of age about $\tilde{\alpha}$ that react into product during time interval $\Delta \alpha$).

\[
VI(\alpha + \Delta \alpha) C_A(\alpha + \Delta \alpha) \Delta \alpha = VI(\alpha) C_A(\alpha) \Delta \alpha \\
- Q \Delta \alpha E(\tilde{\alpha}) C_A(\tilde{\alpha}) \Delta \alpha - VI(\tilde{\alpha}) \Delta \alpha r_{A-} (C_A(\tilde{\alpha})) \Delta \alpha
\]

(71)

Here $r_{A-}(C_A(\tilde{\alpha})) = (-r_A)$ is defined as positive for the rate of disappearance of reactant $A$. It is multiplied by $\Delta \alpha$ since this is the time during which the reaction takes place.

Dividing by $\Delta \alpha^2$ and taking the limit as $\Delta \alpha \to 0$ we get:

\[
\bar{\tau} \lim_{\Delta \alpha \to 0} \frac{I(\alpha + \Delta \alpha) C_A(\alpha + \Delta \alpha) - I(\alpha) C_A(\alpha)}{\Delta \alpha} =
\]

\[
- \lim_{\Delta \alpha \to 0} \{ E(\tilde{\alpha}) C_A(\tilde{\alpha}) \} - \bar{\tau} \lim_{\Delta \alpha \to 0} \{ I(\tilde{\alpha}) r_{A-} (C_A(\tilde{\alpha})) \}
\]

(72)

\[
\bar{\tau} \frac{d}{d\alpha} (IC_A) = -EC_A - \bar{\tau} r_{A-}
\]

\[
\bar{\tau} \frac{dI}{d\alpha} C_A + \bar{\tau} \frac{dC_A}{d\alpha} = -EC_A - \bar{\tau} r_{A-}
\]

\[
-EC_A + \bar{\tau} \frac{dC_A}{d\alpha} = -EC_A - \bar{\tau} r_{A-}
\]

\[
\bar{\tau} \left[ \frac{dC_A}{d\alpha} + r_{A-} \right] = 0
\]

(73)

This is satisfied for all $\alpha$ only if

\[
\frac{dC_A}{d\alpha} + r_{A-} = 0
\]

(74)

Reorganizing this we get:

\[
\{ - \frac{dC_A}{d\alpha} = r_{A-} \}
\]

\[
\alpha = 0 , \quad C_A = C_{A0}
\]

(75)

which is the reactant mass balance in a batch system!
The outflow is now represented by summing and averaging the composition of all side streams that form the exit stream (see Figure 6).

\[
C_{\text{out}} = \int_{0}^{\infty} C_A(\alpha) \ E(\alpha) \ d\alpha
\]  

which is the segregated flow model.

It was Zwietering (Chem. Eng. Sci. 11, 1 (1959)) who realized that the segregated flow model represents one limit on micromixing within the constraints imposed by the RTD of the system, i.e. represents segregation by age and mixing on molecular scale as late as possible, i.e. only at the exit. The necessary conditions for the segregated flow model can then be expressed by the requirement that every point in the system has a delta function age density function \( I_p(\alpha) = \delta(\alpha - \alpha_p) \) so that mixing of molecules of various ages is permitted only at the exit.
3.2 Maximum Mixedness Model

Besides classifying the fluid elements according to their age, one can also group them according to their life expectation, where life expectancy is the time that will elapse between the time of observation of the system and the moment when the fluid element leaves the system. In this manner each fluid element could be characterized by its residence time $t$ so that $t = \alpha + \lambda$. At the entrance, i.e., in the inflow each fluid element has a life expectancy equal to its residence time. The life expectation density function for the elements of the inflow, as seen before, equals the exit age density function $L_s(t) = E(t)$.

Each fluid element of the outflow has zero life expectation and an age equal to its residence time, and the age density function is the density function of residence times. The fluid elements in the system are distributed in their age, $I(\alpha)$, and life expectancy, $L_s(\lambda)$. The number of elements in the system of life expectancy about $\lambda$, $VL_s(\lambda) \, d\lambda$, must equal the number of elements of age $\alpha = \lambda$, $VI(\alpha) \, d\alpha$, if steady state at constant volume is to be maintained. Thus, the life expectation density function of the elements in the system equals the internal age density function $I(\alpha) = L_s(\alpha)$.

We can now view micromixing, i.e., mixing process on small scale down to molecular level, to be a transition of the fluid elements from segregation by age to segregation by life expectation. Namely, at the reactor entrance all fluid elements are segregated by age and have the same age of $\alpha = 0$ and are distributed in life expectation with the density function $E(\lambda)$. At the reactor exit all fluid elements are segregated by life expectation and have life expectation $\lambda = 0$ while they are distributed by age with the density function $E(\alpha)$. The details of this transition from segregation by age to segregation by life expectation could only be described with the complete knowledge of the flow pattern and turbulent fields. However, just like it was possible to describe one limit on micromixing (the latest possible mixing) by the segregated flow model by maintaining segregation by age until zero life expectancy was reached for each element of the system, it is also possible to describe the other limit on micromixing. This other limit of the earliest possible mixing, or the maximum mixedness model, is obtained by requiring that all elements of various ages are assembled (segregated) by their life expectancy. Zwietering suggested and proved (Chem. Eng. Sci. II, 1 (1959)) that the following conditions should be satisfied for the maximum mixedness model.

a) All fluid elements within any point of the system have the same life expectancy, i.e., the point life expectancy density function is a delta function $L_p(\lambda) = \delta(\lambda - \lambda_p)$, and all elements of the point exit together.
b) All points with equal life expectation $\lambda_p$ are either mixed or at least have identical internal age distribution.

These conditions express the requirement that all the elements, which will leave the system at the same time and hence will be mixed at the outflow, are mixed already during all the time that they stay in the system. This means that the elements of the longest residence time are met and mixed constantly with elements of lesser residence times, but which have the same life expectancy and with which they will form the outflow. Schematically the conceptual maximum mixedness model can be described as sketched below.

**FIGURE 7:** Schematic of the Maximum Mixedness Model for Reactant A.

The life expectation scale runs opposite to the volume scale of the system which is counted from the inlet. Thus $dv = -VI(\lambda) d\lambda$ represents the element of reactor volume occupied by the fluid of life expectancy between $\lambda$ and $\lambda + d\lambda$ because at $\lambda = \infty$, $v = 0$ and at $\lambda = 0$, $v = V$.

The model schematically shows that we have distributed the inlet flow according to its life expectation and are mixing it with the fluid of other ages but with the same life expectation.

We can now write a balance on all fluid elements between life expectation $\lambda$ and $\lambda + \Delta\lambda$:

(Elements of the system with life expectancy about $\lambda$ ) =

(Elements of the system with life expectancy about $\lambda + \Delta\lambda$ ) +

(Elements of the inflow of life expectancy about $\tilde{\lambda}$ added to the system during time $\Delta\lambda$ ).
where $\lambda \leq \tilde{\lambda} \leq \lambda + \Delta \lambda$.

Then $VI(\lambda)\Delta \lambda = VI(\lambda + \Delta \lambda)\Delta \lambda + Q\Delta \lambda \ E(\tilde{\lambda})\Delta \lambda$ \hspace{1cm} (77)

Taking the limit as $\Delta \lambda \to 0$ yields:

$$-\tilde{t} \lim_{\Delta \lambda \to 0} \frac{I(\lambda + \Delta \lambda) - I(\lambda)}{\Delta \lambda} = \lim_{\Delta \lambda \to O, \lambda + \Delta \lambda} E(\tilde{\lambda})$$

$$-\tilde{t} \frac{dI}{d\lambda} = E(\lambda)$$ \hspace{1cm} (78)

$$\lambda \to \infty \quad I = 0$$ \hspace{1cm} (78a)

Again we have derived the known relationship between the $I$ and $E$ function.

Let us make now a **balance on all fluid reactant elements between life expectancy $\lambda$ and $\lambda + \Delta \lambda$** (Refer to Figure 7).

(Reactant elements in the system of life expectancy about $\lambda$) =

(Reactant elements in the system of life expectancy about $\lambda + \Delta \lambda$) +

(Reactant elements of life expectancy about $\tilde{\lambda}$ added to the system during time $\Delta \lambda$) -

(Reactant elements of life expectancy about $\tilde{\lambda}$ that have reacted during time $\Delta \lambda$)

$\begin{align*}
VI(\lambda)\Delta \lambda \ C_A(\lambda) &= VI(\lambda + \Delta \lambda) \ C_A(\lambda + \Delta \lambda) \\
&+ Q\Delta \lambda \ E(\tilde{\lambda})\Delta \lambda \ C_{A_0} - VI(\tilde{\lambda})\Delta \lambda \ r_{A_-}(C_A(\tilde{\lambda}))\Delta \lambda
\end{align*}$ \hspace{1cm} (79)

Taking the limit as $\Delta \lambda \to 0$

$$-\tilde{t} \lim_{\Delta \lambda \to 0} \frac{I(\lambda + \Delta \lambda) \ C_A(\lambda + \Delta \lambda) - I(\lambda) \ C_A(\lambda)}{\Delta \lambda} =$$

$$C_{A_0} \lim_{\Delta \lambda \to 0} E(\tilde{\lambda}) - \tilde{t} \lim_{\Delta \lambda \to 0} I(\tilde{\lambda}) r_{A_-}(C_A(\tilde{\lambda}))$$

$$-\tilde{t} \frac{d(I C_A)}{d\lambda} = C_{A_0} E - \tilde{t} r_{A_-}$$
The governing differential equation for the maximum mixedness model is

\[
-\bar{i} \frac{dI}{d\lambda} C_A - \bar{i}I \frac{dC_A}{d\lambda} = C_{A_0} E - \bar{i}I r_{A-}
\]

\[
EC_A - \bar{i}I \frac{dC_A}{d\lambda} = C_{A_0} E - \bar{i}I r_{A-}
\]

\[
\frac{dC_A}{d\lambda} + \frac{E}{\bar{i}I} \left(C_{A_0} - C_A\right) - r_{A-} = 0
\]

or

\[
\frac{dC_A}{d\lambda} = r_{A-} - \frac{E(\lambda)}{W(\lambda)} \left(C_{A_0} - C_A\right)
\] (80a)

This is the governing differential equation for the maximum mixedness model. For elements of extremely large life expectation the change in reactant concentration is small. Therefore, the proper boundary condition is

\[
\lambda \rightarrow \infty \quad \frac{dC_A}{d\lambda} = 0
\] (80b)

In practical applications of the maximum mixedness model one evaluates \(C(\lambda = \infty)\) by implementing condition (80b) into eq. (80a) and solving

\[
\lim_{\lambda \rightarrow \infty} \frac{W(\lambda)}{E(\lambda)} = \frac{C_{A_0} - C_A(\lambda = \infty)}{r_{A-}(C_A(\lambda = \infty))}
\] (81)

Once \(C_A(\lambda = \infty) = C_{A_\infty}\) is obtained from eq (81), eq (80a) can be integrated backwards from \(\lambda = \infty\) where \(C_A = C_{A_\infty}\) to \(\lambda = 0\) where the desired exit reactant concentration \(C_{A_{exit}} = C_A(\lambda = 0)\) is obtained. For numerical integration one cannot use an infinite integration range. Then \(\lambda = 5\bar{t}\) to \(\lambda = 10\bar{t}\) is often chosen to represent infinity \((\lambda = \infty)\) by checking that at such high values of \(\lambda\) the value of \(\frac{dC_A}{d\lambda}\) is almost zero.

Another alternative is to remap \(\lambda \in (0, \infty)\) to \(x[0,1]\) space by a transformation such as

(a) \(x = e^{-\lambda}; \quad \lambda = \ln \frac{1}{x}\) (82a)

or

(b) \(x = \frac{1}{1 + \lambda}; \quad \lambda = \frac{1-x}{x}\) (82b)
This still introduces a singularity at $x = 0$ and special precaution has to be taken to integrate eq (80a) properly.

The maximum mixedness model of Zwietering given by eqs. (80a) and (81) gives us the lower bound on conversion for monotonic rate forms with $\frac{d^2 r}{dC_A} > 0$ and upper bound on conversion for monotonic rates with $\frac{d^2 r}{dC_A^2} < 0$.

Now the segregated flow and maximum mixedness model bound the performance of reactors for all monotonic rate expressions provided the reactor RTD is known. These models are extremely important conceptually. In practice, their use is limited by our inability to know reactor RTDs a priori.

These models can be quite useful in assessing the performance of a CSTR for which by a tracer test it can be proven that there are no stagnancies and no bypassing and that the E-curve is exponential. For water and liquid hydrocarbons the power input is usually sufficient to generate small eddies. Kolmogoroff's isotropic turbulence theory predicts that the microscale of turbulence (i.e the smallest size of turbulent eddies below which turbulent velocity fluctuations are highly damped by molecular viscosity) is given by:

$$\lambda_k = \left(\frac{v^3}{\dot{e}}\right)^{1/4}$$

(83)

where $v = \mu / \rho (cm^2 / s)$ is the kinematic viscosity of the fluid and $\dot{e}$ is the energy dissipated per unit mass. In water $\lambda_k = O(10 \mu m)$. The characteristic diffusion time then is

$$\tau_D = \frac{\lambda_k^2}{D} = \frac{(10^{-3})^2}{10^{-5}} = 10^{-1} s$$

(84)

Water and lower chain hydrocarbons are likely to behave like a microfluid, and a CSTR at sufficient energy dissipation will operate at maximum mixedness condition except for very fast reactions and unpremixed feeds, i.e. for reactions with characteristic reaction time $< 10^{-2} s$.

However in highly viscous polymer systems $\lambda_k = O(100 \mu m)$ or larger and $D = O(10^{-8} cm^2 / s)$. Then $\tau_D = \frac{(10^{-2})^2}{10^{-8}} = 10^4 s$ and a CSTR with a premixed feed
is likely to behave as in a segregated flow mode. Remember, however that if the feed is not premixed segregated flow leads to no conversion.

For a CSTR \( \frac{W(\lambda)}{E(\lambda)} = \bar{r} \) and eq (5a) leads to the condition:

\[
\bar{r} = \frac{C_{Ao} - C_{Ae}}{r_{Ae}(C_{Ae})} \tag{85}
\]

However, since \( E(\lambda)/W(\lambda) = \frac{1}{\bar{r}} \) is independent of \( \lambda \), eq (80a) is satisfied by eq (85) for all \( \lambda \). Therefore \( C_A(\lambda = 0) = C_{Ae} \) and is given by solution of eq (81) which represents the classical ideal reactor design equation for a CSTR mixed on a molecular level. Naturally, the reactant concentration in a perfectly mixed CSTR in all fluid elements is the same and independent of their life expectation.

Thus, for a CSTR, the segregated flow model yields:

\[
C_A = \frac{1}{\bar{r}} \int_{0}^{\infty} e^{-rt} C_{A_{batch}}(t) dt = \int_{0}^{\infty} e^{-\theta} C_{A_{batch}}(\theta) d\theta \tag{86}
\]

and the maximum mixedness model gives

\[
\bar{r} = \frac{C_{Ao} - C_{A}}{r_{Ae}(C_{A})}. \tag{87}
\]

On the other hand for a PFR, the segregated flow model gives

\[
C_A = \int_{0}^{\infty} \delta(t - \bar{r}) C_{A_{batch}}(t) dt = C_{A_{batch}}(\bar{r}) \tag{88}
\]

Maximum mixedness model for a PFR, upon reflection, shows that condition (81) is not valid, and must be replaced, due to the presence of a \( \delta(t - \bar{r}) \left( C_{Ao} - C_A \right) \) in eq (80a), by

\[
\lambda = \bar{r}, \ C_A = C_{Ao} \tag{89}
\]

Then eq (80a) becomes

\[
\frac{dC_A}{d\lambda} = r_{Ae} \tag{90}
\]
If we substitute \( t = \bar{t} - \lambda \) the maximum mixedness PFR equation becomes

\[
\frac{dC_A}{dt} = -r_A,
\]

\( t = 0 \quad C_A = C_{Ao} \) \hspace{1cm} \text{(91)}

and the desired exit concentration is given by \( C_A(\lambda = 0) = C_A(t = \bar{t}) \) which is exactly the expression given above for the segregated flow model.

Because the PFR model and its RTD prohibit mixing of elements of different ages, there is no difference in the prediction of the segregated flow or the maximum mixedness model. They both yield an identical result.

It remains for the reader to show that a first order reaction in a system of any RTD (not that of a CSTR or PFR) yields the same result according to the segregated flow model

\[
C_A = \int_{0}^{\infty} C_{Ao} E(t)e^{-kt} dt
\]

\hspace{1cm} \text{\text{(93)}}

and the maximum mixedness model

\[
\frac{dC_A}{d\lambda} = kC_A - \frac{E(\lambda)}{W(\lambda)} (C_{Ao} - C_A)
\]

\[\lambda \rightarrow \infty \quad \frac{dC_A}{d\lambda} = 0\]

\hspace{1cm} \text{\text{(94)}}

\hspace{1cm} \text{\text{(95)}}

One should note that the function appearing in the above formulation of the maximum mixedness model, i.e. \( E/W \) has special significance, is called the intensity function and is very useful in evaluation of stagnancy or bypassing within the system as described in the previous section.

Fluid passes through the vessel in a regular fashion. The longer the fluid element has been in the vessel (the larger its age) the more probable that it will exit in the next time interval.
Bypassing. Some fluid has increased probability of leaving at a very young age. Rest of the fluid behaves normally.

Stagnancy. After main flow leaves the probability of the fluid caught in dead zones to exit decreases until very large ages are reached at which point all fluid must ultimately leave.

3.3 Other Micromixing Models

Attempts have been made to characterize the intermediate levels of micromixing between the extremes of segregated flow and maximum mixedness by appropriate models. Early on Danckwerts (1951) and later Zwietering (1952) introduced the degree of segregation as a measure of micromixing in the system and proposed ways to evaluate this measure experimentally or to calculate it from the models.

Key Classical References:

Mixing Effects in Chemical Reactors

(CHE 471)

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Mixing Effects in Chemical Reactors—I
—Nonideal Reactors and Tracer Response Analysis

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OBJECTIVES
At the completion of this module the student should be able to:
1. State several causes for deviations from ideal flow conditions in real reactors.
2. Describe an impulse response measurement, and recognize characteristic impulse responses for ideal plug flow, perfect mixing, and dispersed plug flow.
3. Derive the tracer balance equation, state the conditions under which it is valid, and apply it to the measurement of a volumetric flow rate.
4. Define the concept of mean residence time, calculate a mean residence time from a measured impulse response, and use the result to determine a volumetric flow rate or the fluid volume between injection and detection points.
5. Use an impulse response to derive an ideal flow model for a continuous process vessel, and combine the model with a kinetic rate law to determine an expected extent of reaction.

PREREQUISITE MATHEMATICAL SKILLS
1. Differential and integral calculus.

PREREQUISITE ENGINEERING AND SCIENCE SKILLS
1. Understand the concept of a kinetic rate law. Have studied the design and analysis of ideal plug flow reactors and ideal continuous stirred-tank reactors.

A continuous reactor may behave very much like a plug flow reactor or a perfect mixer, but it can never completely achieve either of these ideal states. In an ideal plug flow reactor, all reactant and product molecules at a given axial position move at the same rate in the direction of the bulk fluid flow, while in real flow reactors, fluid velocity profiles, turbulent mixing and molecular diffusion cause molecules to move with a variety of speeds and directions. In an ideal continuous stirred-tank reactor, the reactant concentration is uniform throughout the reaction vessel, while in a real stirred tank, the reactant concentration is relatively high at the point where the feed enters, and low in the stagnant regions that develop in corners and behind baffles.

These inevitable deviations from ideal reactor conditions lead to several fundamental problems in reactor design and analysis:

1. Can an existing or planned reactor be treated as one of the ideal types (PFR or CSTR), or must nonidealities be considered when predicting the conversion which will result from a given feed rate and composition?
2. If nonideals are important, what are they, and how can they be taken into account?

This module, and several that follow it, describe a technique called **tracer response analysis**, which is used to characterize the type of flow and mixing that takes place in a continuous process vessel. The technique is also applicable to biological systems, like organs and blood vessels, to hydrological systems, like rivers and estuaries; in general, to any system through which a fluid flows continuously.

**THE TRACER-RESPONSE TECHNIQUE: QUALITATIVE DISCUSSION**

Suppose the continuous process unit in Figure 1 operates at steady state, and that it is possible to measure the rate at which individual fluid molecules leave the unit in the outlet stream. There is no way to tell what kind of flow and mixing takes place in the unit simply by observing the outlet; fluid molecules leave at a rate equal to the rate at which they enter, whether the unit is an ideal plug flow reactor, an ideal CSTR, or any real unit. Why must this be so?

Suppose, however, that 100 molecules of a different species are abruptly injected at the inlet, and that it is possible to distinguish between these molecules and those of the bulk species at the outlet. For ease of discussion, let us call the molecules of the original species “white,” and those of the injected species, “red.” What would an observer instructed to watch for red molecules at the reactor outlet see?

The rate at which red molecules emerge depends upon the type of flow and mixing in the reactor. In ideal plug flow (Figure 2), all of the molecules would move through at the same velocity, and therefore all would emerge at once, after a time from injection equal to the mean residence time \( t \) in the unit (\( t = \text{tube length/velocity or volume/volumetric flow rate} \)).

On the other hand, in anything but an ideal plug flow reactor, a distribution of residence times would be observed—some red molecules would reach the outlet relatively quickly, emerging at times less than the mean residence time \( t \), while others would remain in the reactor for times considerably longer than \( t \). If the observer at the reactor outlet counts the number of red molecules that emerge in 1 second intervals, he might obtain a curve resembling one of the types shown in Figures 3a, b, and c. The shape of the curve depends strongly on how much mixing takes place in the reactor. In a slightly mixed tubular reactor, some molecules move faster than the mean fluid velocity, and others move slower, but the bulk moves close to the mean velocity and a relatively narrow distribution of residence times results (Figure 3). In a well-mixed system, the red molecules become distributed throughout the reactor relatively quickly, and emerge at a rate proportional to the number contained in the reactor—a high rate initially, when all are contained, and a steadily decreasing rate as the number remaining decreases (Figure 3a). For a reactor which is neither unmixed (PFR), nor perfectly mixed (CSTR), a response resembling that in Figure 3b might be obtained.

What has just been described in a qualitative way, is known as an **impulse response test**. An impulse is an injection that takes place instantaneously. The injected species functions as a tracer. In real experiments, the tracer is a radioactive substance or a dye or any other material whose outlet concentration can easily be measured. The injection at the inlet takes a finite time, but if the time it takes (typically 0.1 second) is much less than the mean residence time in the process unit, it is reasonable to consider it instantaneous. Techniques for analyzing responses to tracer inputs, other than impulses, will be discussed later.

The next section of this module formally introduces some terminology of impulse response testing, and outlines calculations that can be performed using the results of impulse response tests.

**THE TRACER BALANCE EQUATION**

Let us consider a continuous process unit operating at steady-state with a single input and output. In Figure 4, at a time \( t = 0 \), \( m_i \) grams of a tracer are injected into the inflow stream just before the entrance to the unit, and the concentration of tracer in the exit
stream \( c(t) \) [g tracer/liter] is measured as a function of time. The following assumptions are made.

1. The tracer is perfect—i.e., the tracer molecules behave identically to the process fluid molecules within the process unit—and no tracer is lost within the system by reaction or adsorption on the walls.

2. The fluid velocity profiles at the inlet and outlet are flat.

3. The tracer enters and leaves the unit at the bulk inlet and outlet fluid velocities, which is to say the rate of diffusion of the tracer at the inlet and outlet is negligible compared to the rate of bulk convective flow (However, any extent of mixing or diffusion may take place within the unit.). The term closed vessel is used to signify a process unit for which this condition is satisfied. The mass flow rate of tracer at the outlet is

\[
q \text{ [L/min]} \ c(t) \text{ [g/L]} = q c(t) \text{ [g/min]}
\]

In the infinitesimal time interval from \( t \) to \( (t + dt) \), the amount of tracer that leaves the unit is

\[
q c(t) dt \text{ [g tracer]}
\]

If the amounts that leave in each such time interval from \( t = 0 \) to \( t \to \infty \) are summed (integrated), the total must be the total amount of tracer injected, or

\[
\int_0^\infty q c(t) dt = \int_0^\infty c(t) dt = m_i \tag{1}
\]

Equation 1 is a fundamental relationship in tracer response analysis. The integral of \( c(t) \) can be determined by numerically integrating the experimental response curve (see Appendix). If both \( q \) and \( m_i \) are known independently, Equation 1 functions as a material balance (tracer out = tracer in); if it is not satisfied, then the assumption that tracer is not lost due to adsorption or reaction is invalid. If only \( m_i \) is known and the tracer is indeed conserved, Equation 1 may be used to determine the volumetric flow rate \( q \). This technique has been used to measure flow rates in conduits ranging in size from blood vessels to rivers.

**Example 1: Flow Rate Measurement Using a Tracer Balance**

10 mg of a dye are injected at the inlet of a continuous reactor. Small samples are then periodically withdrawn from the reactor outlet stream, and the dye concentrations in the samples are measured using a photometer. The response curve shown in Figure 5 is obtained. The area under the curve determined by numerical integration is 7.5 (mg/L) \cdot \text{min}. What is the volumetric flow rate? If the reactor volume is 10 liters, what is the mean residence time in the reactor?

**Solution:**

From Equation 1,

\[
q = \frac{m_i}{\int_0^\infty c(t) dt} = \frac{10 \text{ mg}}{7.5 \text{ mg} \cdot \text{min/L}} = 1.33 \text{ L/min}
\]

\[
\bar{t} = \frac{V}{q} = \frac{10 \text{ L}}{1.333 \text{ L/min}} = 7.5 \text{ min}
\]

It can be seen from the shape of the output curve that this process vessel cannot be considered an ideal PFR or CSTR (see Figure 3).

**MEAN RESIDENCE TIME**

If a total of four tracer molecules were injected at the inlet of a process unit, and one emerged after one minute, two after two minutes, and the last one after three minutes, the average residence time for all four molecules would be

\[
\bar{t} = \frac{(1 \times 1 \text{ min}) + (2 \times 2 \text{ min}) + (1 \times 3 \text{ min})}{1 + 2 + 1} = 2 \text{ min}
\]

The mean residence time of the tracer molecules in the impulse response test described in the preceding section can be obtained in a similar manner. The number of tracer molecules that emerge in the time interval from \( t \) to \( (t + dt) \) is

\[
dm_i = q \text{ [L/min]} \ c(t) \text{ [g/L]} \ dt \text{ [min]}
\]

The mean residence time is

\[
\bar{t} = \frac{\int_0^\infty t dm_i(t)}{\int_0^\infty dm_i(t)}
\]

Substitute for \( dm_i \),

\[
\bar{t} = \frac{\int_0^\infty t c(t) dt}{\int_0^\infty c(t) dt} \tag{2}
\]

Equation 2 gives the mean residence time for tracer molecules in the process unit, but since we have assumed that the tracer molecules behave identically to the process fluid molecules, \( \bar{t} \) must also be the mean residence time for all molecules in the unit.

We have not shown that \( \bar{t} \) determined from Eq. (2) is equal to the previously defined value of the mean residence time, \( \bar{V} \text{[liters]} / \bar{q} \text{[liters/second]} \). We will temporarily assume that this is the case, and prove it in a later module when the concept of age distributions.
is introduced. Therefore

\[
\bar{t} = \frac{\int_0^\infty \frac{t}{c(t)} dt}{\int_0^\infty c(t) dt}
\]

(3)

The right-hand side of Equation 3 can be calculated by numerical integration of a measured impulse response to yield \( \bar{t} \) directly. If the reactor volume \( V \) is known, \( q \) may then be determined, and conversely the volume may be calculated from a known value of \( q \). Notice that this method of determining \( q \) (unlike the method of Equation 1) does not require a knowledge of the amount of tracer injected; also, any measured signal proportional to \( c(t) \) may be used directly in place of \( c(t) \) itself. (Why?)

**Example 2: Determination of Mean Residence Time**

A tracer is injected at the inlet of a process unit, and the response in Figure 6 is obtained.

\[
c(t) = \begin{cases} 
0.1 & 1 \leq t \leq 2 \\
0.1 & 2 \leq t \leq 3 \\
0 & \text{everywhere else}
\end{cases}
\]

(The form of the response was chosen for illustrative purposes; real tracer responses never look like this.) Calculate the mean residence time in the reactor. If the reactor volume is 2 liters, what is the volumetric flow rate of the fluid passing through it?

**Solution:**

\[
\int_0^\infty c(t) dt = \frac{1}{2} (2)(0.1) = 0.1 \text{ (g/cm}^3) \cdot \text{min}
\]

\[
\int_0^\infty tc(t) dt = 0.1 \int_1^2 t(t-1) dt + 0.1 \int_2^3 t(3-t) dt = 0.2 \text{ (g/cm}^3) \cdot \text{min}^2
\]

so that,

\[
\bar{t} = \frac{\int_0^\infty tc(t) dt}{\int_0^\infty c(t) dt} = 2 \text{ min}
\]

![Figure 6. Impulse response (Example 2).](image)

\[q = \frac{V}{\bar{t}} = \frac{20 \text{ L}}{2 \text{ min}} = 10 \text{ L/min}\]

**NOMENCLATURE**

- \( c \): tracer concentration measured in the outflow of the system
- \( m_t \): mass of tracer injected in an impulse injection
- \( q \): volumetric flow rate through the system
- \( t \): time
- \( \bar{t} \): mean residence time
- \( V \): volume of the system

**LITERATURE CITED**


**STUDY PROBLEMS**

1. Why are the conditions of ideal plug flow and perfect mixing never achieved in real reactors, however closely they may be approached?

2. What is a perfect tracer? A closed vessel? An impulse injection?

3. If a tracer impulse is injected at the inlet of an ideal plug flow reactor and the tracer concentration at the outlet is measured and plotted as a function of time from injection, what would the plot look like?

4. Repeat Question 3 for an ideal CSTR. Explain the shape of the response.

5. The following tracer impulse responses were obtained for continuous reactors. In each case, indicate whether you would model the reactor as an ideal PFR, an ideal CSTR, or neither.

**Response 1.**

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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<td>1.4</td>
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**Response 2.**

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<th>2.1</th>
<th>2.2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.01</td>
<td>10.0</td>
<td>0.02</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

**Response 3.**

<table>
<thead>
<tr>
<th>( t )</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c )</td>
<td>1.0</td>
<td>3.0</td>
<td>6.3</td>
<td>4.7</td>
<td>2.6</td>
<td>1.8</td>
<td></td>
</tr>
</tbody>
</table>

6. According to Equation 1,

\[
\int_0^\infty qc(t) dt = m_t
\]

where \( m_t \) is the total mass of tracer injected in an impulse test. Suppose a response obtained using a
radioactive tracer in a very long channel is integrated numerically, and it is found that

\[ \int_0^t q(t)dt < m_i \]

Suggest an explanation for this result which might be true for any tracer, and a second explanation applicable specifically to a radioisotope.

7. Ten grams of a tracer are injected at the inlet of a reactor. Samples are withdrawn at the outlet and the concentration of the tracer in each sample is measured. The results are shown in Figure 7. The area under the curve is determined by numerical integration to be 50 mg·s/mL. What is the volumetric flow rate of fluid in the reactor? If the reactor volume is 10 liters, what is the mean residence time in the reactor?

8. How could you calculate \( r \) from the experiment of Question 7 without knowing the quantity of tracer injected?

**HOMEWORK PROBLEMS**

1. In Figure 8, a process fluid passes through a continuous tubular reactor with a 3 cm inner diameter. One gram of a tracer is injected instantaneously at the reactor inlet, and the following symmetrical outlet response is measured at a point 175 cm from the injection point.
   a) Is this reactor closer to being an ideal plug flow reactor or a perfect mixer?
   b) Calculate the volumetric flow rate using the tracer balance equation.
   c) Calculate the volumetric flow rate by first calculating the mean residence time.

2. Consider the following simplified biomedical experiment performed on a dog’s kidney which is being artificially perfused by a pump at a constant flow rate of 100 mL/min. Two tracers are injected in the inflow and their concentrations are monitored in the major vein leaving the kidney. Tracer 1 cannot penetrate across the walls of the blood vessels and remains confined to the blood. Tracer 2 readily penetrates through all the fluids and tissues of the kidney but is not removed by urine. Ten grams of each tracer are injected at time \( t = 0 \) and an idealized response is presented Figure 9. Find the volume of distribution of tracer 1 (blood volume, \( V_i \)), and of tracer 2 (total kidney volume, \( V_k \)). Assume that the partition coefficient for tracer 2 is one, i.e. that the tracer is equally soluble in all kidney fluids.

3. An impulse response test is performed on a continuous reactor. The following is measured.

<table>
<thead>
<tr>
<th>time from injection (t seconds)</th>
<th>tracer concentration in outlet stream (( \text{mg/L} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.400</td>
</tr>
<tr>
<td>10</td>
<td>0.383</td>
</tr>
<tr>
<td>15</td>
<td>0.367</td>
</tr>
<tr>
<td>20</td>
<td>0.353</td>
</tr>
<tr>
<td>25</td>
<td>0.338</td>
</tr>
<tr>
<td>30</td>
<td>0.325</td>
</tr>
<tr>
<td>60</td>
<td>0.253</td>
</tr>
<tr>
<td>90</td>
<td>0.197</td>
</tr>
<tr>
<td>120</td>
<td>0.153</td>
</tr>
<tr>
<td>150</td>
<td>0.119</td>
</tr>
<tr>
<td>180</td>
<td>0.093</td>
</tr>
<tr>
<td>310</td>
<td>0.072</td>
</tr>
<tr>
<td>340</td>
<td>0.056</td>
</tr>
<tr>
<td>370</td>
<td>0.044</td>
</tr>
<tr>
<td>300</td>
<td>0.034</td>
</tr>
<tr>
<td>330</td>
<td>0.027</td>
</tr>
<tr>
<td>360</td>
<td>0.021</td>
</tr>
<tr>
<td>390</td>
<td>0.016</td>
</tr>
<tr>
<td>420</td>
<td>0.013</td>
</tr>
<tr>
<td>450</td>
<td>0.010</td>
</tr>
<tr>
<td>480</td>
<td>0.008</td>
</tr>
<tr>
<td>510</td>
<td>0.006</td>
</tr>
</tbody>
</table>

\( \Delta t = 5 \text{ seconds} \)

\( \Delta t = 30 \text{ seconds} \)

a) Extrapolate the data back to the \( c \) axis to estimate the value of \( c \) at \( t = 0 \), and calculate the mean residence time in the reactor, either by graphical integration or using the computer program in the Appendix.

b) If the volumetric flow rate in this experiment was 4 L/min, what is the reactor volume, and how much tracer was injected?

c) Suppose a first-order reaction \( A \rightarrow B \), \( k = 0.5 \) \text{ min}^{-1} \) is carried out in the reactor with the same volumetric flow rate used in the impulse response test. Use the results of Part (a) to choose and

---

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evaluate the parameters of an ideal reactor model, and calculate the fractional conversion of A which would be achieved in the reactor.

Notes: 1. If \( \bar{t} \) is calculated using the computer program, you will have to apply the program twice for each integral from \( t = 0 \) to \( t = 510 \) seconds—once for \( 0 \leq t \leq 30 \), and again for \( 30 \leq t \leq 510 \).
2. The true response continues to \( t \rightarrow x \).
   A truncation error is introduced when the response is cut off at \( t = 510 \) seconds; this is an unavoidable error in any tracer response experiment.

APPENDIX: SIMPSON'S RULE FOR NUMERICAL INTEGRATION

Suppose one wished to calculate

\[ I = \int_{x_1}^{x_n} y(x)dx \]

where \( y(x) \) is a plotted or tabulated function, as in Figure 10.

- \( x \)
- \( y \)
- \( a = x_1 \)
- \( y_1 \)
- \( x_2 \)
- \( y_2 \)
- \( x_3 \)
- \( y_3 \)
- \( x_4 \)
- \( y_4 \)
- \( b = x_5 \)
- \( y_5 \)

Numerical integration is a procedure whereby simple analytical functions are fit to adjacent data points, and these approximate functions are integrated analytically to estimate the area under the true curve. If lines are fit to adjacent pairs of data points, the procedure is called the trapezoidal rule. If instead, parabolas are fit to adjacent triplets of equally spaced points, the procedure is Simpson's rule.

The area under a parabola through three points, whose \( x \) values are separated by a distance \( h \) (see Figure 11), is \( (h/3)[y_1 + 4y_2 + y_3] \). Using this result, it is easy to show (see Figure 12) that the area under \( n \) equally spaced points (note: \( n \) must be odd) is

\[ I = \frac{h}{3} \left[ (y_1 + 4y_2 + y_3) + (y_3 + 4y_4 + y_5) + \ldots + (y_{n-2} + 4y_{n-1} + y_n) \right] \]

or Simpson's rule formula, which is:

\[ \int_{x_1}^{x_n} y(x)dx \approx \frac{h}{3} \left[ y_1 + y_n + 4(y_2 + y_4 + \ldots + y_{n-1}) + 2(y_3 + y_5 + \ldots + y_{n-2}) \right] \]

For example, suppose it is desired to estimate the integral

\[ I = \int_{1}^{5} c(t)dt \]

from the following tabulated data:

<table>
<thead>
<tr>
<th>( t )</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c(t) )</td>
<td>5</td>
<td>12</td>
<td>31</td>
<td>68</td>
<td>129</td>
</tr>
</tbody>
</table>

Then \( n = 5 \), \( h = 1 \), and

\[ \int_{1}^{5} c(t)dt \approx \frac{1}{3} \left[ 5 + 129 + 4(12 + 68) + 2(31) \right] = 172 \]

The integral of any function of \( c \) and \( t \), such as

\[ \int_{1}^{5} tc(t)dt \]

could easily be calculated by determining this function for each entry in the data table, and substituting the calculated values in the Simpson's rule formula.

COMPUTER PROGRAM

Program Name: SIMPR
Language: FORTRAN IV
Object: Evaluate

\[ F_n = \int_{x_1}^{x_n} y(t)dt \]
and
\[ F_1 = \int_{x_1}^{x_n} x y(x) \, dx \]

using Simpson's rule for an array of equally-spaced points \( x_1, x_2, \ldots, x_n \). If \( n \) is even, the program uses Simpson's rule for the interval from \( x_1 \) to \( x_{n-1} \), and the trapezoidal rule for the interval from \( x_{n-1} \) to \( x_n \). The program calculates and prints out \( F_0, F_1, \) and \( F_1/F_0 \).

The following data must be supplied:
- \( NDS \) = Number of sets of \( y(x) \) data for which the program is to be run, and for each data set.
- \( N \) = Number of points.
- \( X(1) \) = First \( x \) value (\( x_1 \)).
- \( H \) = Difference between successive \( x \) values.
- \( Y(1), Y(2), \ldots, Y(N) \) = Dependent variable values (\( y_1, y_2, \ldots, y_n \)).

### Data Format

- Card 1: NDS (Format 110)
- Card 2: \( N, X(1), H \) (Format 110, 2F10.3)
- Card(s) 3, 4, ..., \( Y(1), Y(2), \ldots, Y(N) \) (Format 8E10.3) for each data set

### Example

Impulse response data for a continuous reactor are as follows.

<table>
<thead>
<tr>
<th>( t )</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>9</th>
<th>11</th>
<th>13</th>
<th>15</th>
<th>17</th>
<th>19</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c )</td>
<td>0</td>
<td>2</td>
<td>5</td>
<td>9</td>
<td>8</td>
<td>6.5</td>
<td>4.5</td>
<td>2.0</td>
<td>0.5</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Calculate

\[
F_0 = \int_{1}^{9} c \, dt = \int_{1}^{9} c \, t \, dt
\]

\[
F_1 = \int_{1}^{19} c \, dt = \int_{1}^{19} c \, t \, dt
\]

\[
\hat{t} = F_1/F_0
\]

Input data: (All numbers in fields of 10, integers right-adjusted)

- Card 1: 1
- Card 2: 10 1.0 2.0
- Card 3: 0.000 2.000 5.000 9.000 8.000 6.500 4.500 2.000
- Card 4: 0.500 0.000

---

C *** PROGRAM SIMFR
C *** EVALUATE INTEGRALS OF Y*DX (=F0) AND X*Y*DX
C *** (=F1) FROM X(1) TO X(N)
DIMENSION X(201), Y(201), YC(201)
C *** IF N EXCEEDS 201, INCREASE THE DIMENSIONS OF X,
C *** Y AND YC
READ(1,1) NDS

1 FORMAT(110)
WRITE(3,2) NDS
2 FORMAT(11,13.5X)PROGRAM SIMFR//'//1X13.' DATA
* SET(S) TO BE ANALYZED'/*2X'INPUT DATA'//8X,
* 'X',8X,Y,A(12X,'',6X,'Y')
DO 500 JJ=1,NDS
READ (1,3) N,X(1),H
3 FORMAT(11,2F10.0)
READ(1,4)Y(J), J=1,N
4 FORMAT(*E10.0)
35 DO 40 J=2,N
40 X(J)=X(J-1)+H
WRITE(3,5)X(J),Y(J), J=1,N
5 FORMAT(4X,F7.2,2X,E10.3,3X,F7.2,2X,E10.3,3X,F7.2,2X,
* E10.3,3X,F7.2,2X,E10.3,3X,F7.2,2X,E10.3)
IF(N(N)=N-1) DO 70
KODD=1
NF=N-1
70 CALL SIMP(Y,NF,H,F0)
DO 80 J=1,N
80 Y(J)=Y(J)*Y(J)
CALL SIMP(YC,NF,H,F1)
GO TO (100,90),KODD
90 F0=F0+0.5*H*(Y(NF)+Y(N))
F1=F1+0.5*H*(YC(NF)+YC(N))
100 FR=F1/F0
WRITE(3,6)F0,F1,FR
6 FORMAT(1HG3.5,X,F0 =',E12.5//4X,F1 =',E12.5//
* 4X,F1/F0 =',E12.5)
500 CONTINUE
WRITE(3,7)
7 FORMAT('1')
STOP
END

SUBROUTINE SIMP(Y,N,H,F)
DIMENSION Y(N)
NM1=N-1
NM2=N-2
S1=0.0
DO 100 J=2,NM1,2
100 S1=S1+Y(J)
S2=0.0
DO 200 J=3,NM2,2
200 S2=S2+Y(J)
F=H*(Y(1)+Y(N)+4.0*S1+S2+S2)/3.0
RETURN
END

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1. Departures from ideal plug flow are caused by nonuniform velocity profiles, turbulent mixing and molecular diffusion. Departures from perfect mixing are caused by spatial inhomogeneities at the reactor inlet and stagnant regions in corners and behind baffles.

2. Perfect tracer: tracer molecules behave identically with the process fluid molecules within the process unit.

Closed vessel: rate of diffusion across the vessel entrance and exit boundaries is negligible compared to the rate of convective motion across the boundaries.

Impulse injection: takes place instantaneously (or nearly instantaneously on the time scale of the process).

3. 

4.
The tracer is instantly dispersed throughout the reaction vessel, before any has a chance to emerge. The concentration of tracer in the outlet stream is proportional to the amount of tracer in the vessel; since this quantity has its maximum value at t=0 and thereafter declines, the shape of the response curve follows the same pattern.

5. (a) ideal CSTR; (b) ideal PFR; (c) neither

6. (a) irreversible adsorption on or reaction with the vessel walls
   (b) activity decay

7. \[ q \int c(t) \, dt = m_i \]
   \[ q = \frac{10000 \text{ (mg)}}{50 \text{ (mg/s/mL)}} = 200 \text{ (mL/s)} = \boxed{0.2 \text{ (L/s)}} \]
   \[ \bar{t} = \frac{10 \text{ (L)}}{0.2 \text{ (L/s)}} = \boxed{50 \text{ (s)}} \]

8. Calculate the first moment of the response, and then determine \( \bar{t} \) as
   \[ \bar{t} = \frac{\int_0^\infty tc(t) \, dt}{\int_0^\infty c(t) \, dt} \]
Mixing Effects in Chemical Reactors—II
—Models for Nonideal Reactors

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OBJECTIVES
At the completion of this module, the student should be able to:
1. Understand the necessity for developing approximate models for nonideal reactors; itemize the flow models most often used to model continuous reactors; and recognize the forms of the impulse responses associated with each model.
2. Formulate and apply reactor models which account for stagnancy and channeling; quantifying the models on the basis of impulse response data.

PREREQUISITE MATHEMATICAL SKILLS
1. Understanding of semilogarithmic plots.
2. First-order differential equations.

PREREQUISITE ENGINEERING AND SCIENCE SKILLS
1. Design and analysis of ideal plug flow reactors and ideal continuous stirred tank reactors. Impulse response measurements (Module E4.4).

The following problem statement is missing one important item of information—see if you can identify it.

"A reaction $A \rightarrow B$ whose rate law is $r = 0.05 C_A$ is carried out in a continuous isothermal reactor. The feed rate is 200 L/min and the concentration of $A$ in the feed is 3.0 (mol/L). Calculate the reactor volume required to achieve a fractional conversion of 0.90."

The missing information, without which the problem cannot be solved, is the reactor type. If it were given that the reactor was either an ideal plug flow reactor (PFR) or an ideal continuous flow stirred tank reactor (CSTR), one would have no trouble solving the problem by writing the appropriate material balance equation and solving it for $V$.

Suppose, however, that the reactor is neither an ideal PFR nor an ideal CSTR. In principle, the calculation would be performed in the same manner—by writing and solving the reactor material balance equation. The problem is that for a nonideal reactor, this is more easily said than done. In a perfect mixer, the concentrations of all species are uniform, and the balance is a simple (or at least relatively simple) algebraic equation, and in an ideal plug flow reactor, the only variation is in the axial direction, and the balance equation contains nothing worse than a first derivative. In a nonideal reactor, however, reactant concentrations may vary in all directions; radially, as well as axially, in a tubular flow reactor, and arbitrarily with position in an imperfectly-mixed stirred tank; moreover, reactants move by diffusion, as well as by convection, in any direction in which spatial variations occur. The balance equation for a reactor in which all of these phenomena are taking place is a partial differential equation containing both first and second derivatives. The equation is not particularly hard to derive if enough assumptions are made (3), but it is frequently not clear what boundary conditions to apply; solutions are difficult or impossible to achieve (even using a computer), and generalizations of the results for design and scaleup calculations are usually out of the question.

What is done instead is to formulate a model for the nonideal reactor; a mathematical representation of the
unit which accounts to some extent for observed
departures from ideal reactor conditions, but which
can be analyzed without too much difficulty in order
to derive relations between input and output variables.
A powerful approach to nonideal reactor modeling is
to perform an impulse response test on a flow unit,
and to compare the measured response with responses
characteristic of various relatively simple types of flow
systems. When a correspondence is achieved, the
simple system is used to model the real reactor.

The principal features of several of the most
common flow reactor models, including their charac-
teristic impulse responses, are given in the sections that
follow. In the figures to be shown, the impulse
injection is presumed to take place at a time \( t = 0 \), and
\( \bar{t} \) is the nominal mean residence time in the flow unit:
\[
\bar{t}(s) = \frac{V(m^3)}{q(m^3/s)}
\]
(1)
where \( V \) is reactor volume occupied by the reaction
mixture and \( q \) is volumetric flow rate through the
reactor.

**IDEAL REACTOR MODELS: IDEAL PLUG FLOW
AND PERFECT MIXING**

These models, which by now should need no
description, represent the extreme in simplicity. Their
impulse responses (concentration curves of the tracer
measured at the outflow in response to an instan-
taneous tracer injection in the inflow) are illustrated in
Figures 1a and 1b, where \( R(t) \) is the response propor-
tional to the outlet concentration curve.

If an experimental impulse response appears as a
sharp spike, the flow unit may be modeled as an ideal
plug flow reactor with a mean residence time equal to
the time at which the spike emerges, and if the
response rises almost instantaneously and decays
slowly, the unit may be considered a perfect mixer. It
is not difficult to show that the impulse response of a
perfect mixer is given by the formula
\[
R(t) = R_a \exp \left( -t/\bar{t} \right)
\]
(2)
(see Homework Problem 4) so that a plot of \( \ln R \)
versus \( t \) (or a semilog plot of \( R \) versus \( t \)) should be a
straight line with a slope of \(-1/\bar{t}\). We will illustrate
the application of this formula in the next section.

**STAGNANCY**

In any process unit with corners, baffles, or obstruc-
tions to flow, stagnant regions occur (Figure 2). When
a tracer is injected into a unit where such a zone exists,
some of the tracer diffuses into the zone and is slowly
washed out (Figures 2a, 2b and 2c); the consequence is a
long shallow tail in the response (See Figure 3). In the
extreme case of the phenomenon, the stagnant region
does not participate at all in the process taking place
in the flow unit. The total volume \( V \) of the unit may
then be divided into two regions as shown in Figure 4:
an active region (volume \( V_a \)), through which all the
flow passes, and a stagnant region, or dead volume
(volume \( V_s = V - V_a \)), which simply occupies space in
the unit. The impulse response for this model is that of
the active region alone. The apparent mean residence
time equals \( V_a/q \) and so is less than the nominal mean
residence time \( \bar{t} = V/q \); if the unit is a reactor, the
conversion achieved is therefore lower than the
conversion which the unit was designed to achieve. See

![Figure 2a.](image)

![Figure 2b.](image)

![Figure 2c.](image)

![Figure 3.](image)

![Figure 4.](image)
Figure 5, which shows that the actual mean residence time is smaller than the design value.

**Example: Determination of Stagnancy In a CSTR**

The product yield from a continuous stirred-tank reactor is lower than the design specification calls for, and imperfect mixing is suspected to be the cause. A tracer impulse is injected at the tank inlet, and the response shown in Figure 6 is obtained at the outlet. The tank volume is 2.5 m³, and the volumetric flow rate of the fluid is 2.0 m³/min. Determine whether a stagnant region exists, and if so, what fraction of the tank it occupies.

**Solution:**

It was previously observed that, for a perfect mixer, a plot of log R versus t should yield a straight line with slope $-1/i$. Suppose that the measured response plotted in this manner is as follows (Figure 7). The shallow tail suggestive of a stagnant region appears clearly when the response is plotted in this manner, and the linearity of the earlier portion of the plot suggests that the active portion of the reactor behaves like a perfect mixer. The reactor can therefore be modeled as a perfect mixer and a dead volume (See Figure 4 again). The slope of the line corresponding to the active volume response is

$$\frac{-1}{i_{active}} = \frac{a}{V_a}$$

$$\ln \left( \frac{100}{100} \right) = -1.047 \text{ (min}^{-1}) = \frac{-2(\text{m}^3/\text{min})}{V_a(\text{m}^3)}$$

The effective mean residence time of the unit is therefore only $(1/1.047) = 0.96$ min instead of the design value, $(2.5 \text{ m}^3)/(2.0 \text{ m}^3/\text{min}) = 1.25$ min. This fact could very well account for the low reactant conversion.

The effective active volume may be determined as

$$V_a = \frac{2(\text{m}^3/\text{min})}{1.047 (\text{min}^{-1})} = 1.91 \text{ m}^3$$

so that the fraction of the reactor which is active is

$$\frac{1.91 \text{ m}^3 \text{ (active)}}{2.5 \text{ m}^3 \text{ (total)}} = 0.764$$

Thus, almost 1/4 of the reaction volume does not participate in the process. This result suggests that increasing the stirrer speed, modifying the design of the baffles, or relocating the inlet and outlet ports to reduce the degree of stagnancy in the unit might remedy the problem.

**CHANNELING**

Just as stagnant pockets of fluid may have relatively long residence times in a reactor, it is possible for a portion of fluid entering a reactor to have an anomalously short residence time, a phenomenon known as channeling. Imperfect packing (Figure 8a) in a fixed bed reactor is one possible cause of this phenomenon; overly close placement of the inlet and outlet of a CSTR (Figure 8) is another. A tracer impulse injected at the inlet of one of these units would emerge in two peaks, the first corresponding to the channeling fluid and the second to the bulk fluid (Figure 9).

A model for a system of this sort would consist of two parallel branches, one corresponding to the bulk
fluid and the other corresponding to the channel (Figure 10). The shapes of the response peaks would suggest the type of unit to be inserted into each stream—ideal plug flow, perfect mixing, or one of the nonideal types still to be discussed. If the first response peak emerges almost instantaneously relative to the bulk fluid peak, the unit may be modeled as a single unit with a bypass stream (Figure 11). In any case, the fraction of the fluid which bypasses the main unit may be estimated as the ratio of the area under the bypass peak to the area under the total response curve. Remember \( \int_0^\infty c(t)dt = m_i/\dot{Q} \) is the total area under the curve (why?). Thus the two individual areas above yield the fraction of the fluid that goes through the bypassing and through the main stream since the tracer behaves and distributes itself everywhere as the carrier fluid.

**Example 2: Formulation of a Two-Region Model for a Packed Bed Reactor**

An irreversible first-order reaction \( A \rightarrow B \) is carried out in a packed-bed reactor. A conversion of 74\% was predicted for a feed rate of 15 L/s, but the measured conversion is only 70\%. An impulse response performed on the reactor yielded the following result. See Figure 12. From batch reactor measurements, the rate of reaction per unit void volume is

\[-r_A (\text{mol/L} \cdot \text{s}) = 0.04 \ C_A \]

where \( C_A (\text{mol/L}) \) is the reactant concentration. The void volume in the reactor is 500 liters, and the concentration of \( A \) in the feed is \( C_{A0} = 2 \ (\text{mol/L}) \).

---

**Solution:**

a) The expected conversion in the reactor based upon an assumption of ideal plug flow.

\[ \bar{\tau} = \frac{500 \ L}{15 \ L/s} = 33.3 \ (\text{s}) \]

The ideal PFR design equation is

\[ \bar{\tau} = \frac{1}{r_A} \int_{C_{A0}}^{C_{A}} \frac{dC_A}{-0.04 \ C_A} \]

\[ \rightarrow \]

\[-0.04 \bar{\tau} = \ln \left( \frac{C_{A}}{C_{A0}} \right) \]

\[ \bar{\tau} = 33.3 \ (\text{s}) \]

\[ C_{A0} = 2 \ (\text{mol/L}) \]

\[ C_A = C_{A0} \exp (-0.04 \cdot 33.3) = 0.527 \ (\text{mol/L}) \]

A conversion

\[ x_A = \left( 1 - \frac{C_A}{C_{A0}} \right) = 0.74 \]

is thus predicted assuming ideal plug flow.

b) The shape of the impulse response suggests modeling the reactor as two plug flow reactors in parallel. In Figure 13 the fraction of the total flow that passes through the first reactor—for which \( \bar{\tau} = 15 \) seconds—is \( 20/(20+60) = 0.25 \). In the reactor with smaller residence time, \( q_1 = (0.25\times 15=L/s) = 3.75 \ (L/s) \). The concentration of \( A \) in the exit stream from this reactor is

\[ C_{A1} = C_{A0} \exp (-0.04 \bar{\tau}_1) \]

\[ = 2 \exp (-0.04 \times 15) = 1.10 \ (\text{mol/L}) \]

Similarly, for the second reactor, \( q_2 = (0.75\times 15.00) = 11.25 \ (L/s) \), and

\[ C_{A2} = C_{A0} \exp (-0.04 \bar{\tau}_2) \]

\[ = 2 \exp (-0.04 \times 40) = 0.404 \ (\text{mol/L}) \]

A material balance on \( A \) at the mixing point yields

\[ q_1 C_{A1} + q_2 C_{A2} \]

\[ \rightarrow \]

\[ C_{A'} = \frac{(3.75)(1.10) + (11.25)(0.404)}{15} = 0.577 \ (\text{mol/L}) \]
The predicted conversion is
\[ x_a = 1 - \frac{0.577}{2} = 0.71 \]
or less than that predicted by the single ideal plug flow reactor model. The small remaining difference between the predicted conversion (0.71) and that actually measured (0.70) could be due to phenomena neglected in the two reactor model—intraphase diffusion and mass transfer between phases.

**DISPERSION**

When a slug of a tracer or a reactant enters a flow reactor, only in the case of ideal plug flow does the material in the slug pass through and emerge at nearly a single instant of time. Generally, velocity variations, molecular diffusion and (if the Reynolds number is high enough) turbulent mixing all tend to spread the tracer axially about its center of mass, so that the response signal downstream of the injection point appears as in Figure 14. The term axial dispersion is used to denote this axial spreading, regardless of its origin.

The symmetrical impulse response shown above is representative of units with slight degrees of dispersion—relatively close to ideal plug flow. In flow units with a high degree of axial dispersion, the flow pattern is closer to that of a perfect mixer—the impulse response rises rapidly and falls off slowly, as in Figure 15.

Two models are commonly used to simulate systems with varying degrees of axial dispersion. We will briefly describe them in the following sections, and discuss one of them in greater detail in Module E4.6.

**Dispersion Model**

The fluid flowing through the unit in Figure 16 is assumed to be in plug flow (that is, all radial variations in velocity and concentration are neglected) and the spread in the impulse response is accounted for by superimposing diffusion in the axial direction with an effective diffusivity \( D_e \) (called the axial dispersion coefficient). When \( D_e = 0 \) the model reduces to ideal plug flow, since no axial dispersion remains and a flat velocity profile was assumed. When \( D_e \rightarrow \infty \) axial dispersion dominates over the convective movement of fluid. The mixing due to dispersion is much faster than the movement of the plug flow front, so that the contents of the tube are well mixed and the conditions in a perfect mixer (CSTR) are approached.

**Tanks-in Series Model**

One may recall that a series of \( N \) perfect mixers has a conversion versus total residence time relationship, between that of a single perfect mixer and that of an ideal plug flow reactor. Thus, by using a series of tanks (Figure 17) to represent a flow unit and letting the number of tanks vary from 1 to infinity (while keeping the total volume fixed), one can simulate any degree of axial dispersion, from perfect mixing (\( N = 1 \)) to ideal plug flow (\( N = \infty \)).

In summary, impulse responses for flow systems with varying degrees of axial mixing appear as shown in Figure 18.

Equations and applications for the dispersion model will be developed in a later module (E4.6). For now, one should be able to recognize when they are applicable, and by inspection of an impulse response, one should be able to characterize a system as slightly dispersed, moderately dispersed or highly dispersed.

**RECYCLE MODEL**

Suppose a portion of the output of an ideal PFR (Figure 19) is recycled back to the inlet, with
\[ \Psi = \text{(volume recycled) / (volume withdrawn as product)} \]
As \( \Psi \) the recycle ratio approaches infinity, the recirculation rate is high enough so that the reactant and product concentrations approach uniformity in the reactor; the system then functions as a perfect mixer. Consequently, as the recycle ratio varies from \( \Psi = 0 \) (no recycle) to \( \Psi \rightarrow \infty \) (nearly complete recycle), the reactor behavior varies from plug flow to perfect mixing.

The response of an ideal PFR with recycle to an impulse injection is quite different from the other responses we have seen so far. After the injection some tracer emerges after one mean residence time, and the rest is recycled; additional tracer emerges after another mean residence time elapses (but less tracer than appeared the first time); still more emerges after a third residence time elapses, and so forth. The impulse response appears as shown in Figure 20, where \( \bar{t} = V / q \).
as usual. (Why is the mean residence time for the first pass through the reactor \( \frac{t_f}{(N+1)} \), rather than \( t_f \)?)

A generalized recycle model can be formulated by replacing the ideal PFR with a nonideal reactor model (dispersed plug flow, or tanks-in-series). The impulse response for such a model would appear as in Figure 21.

Reactors with internal circulation (in particular, stirred tanks) often exhibit behavior of this sort. Consequently, the recycle model is a powerful tool for simulating such systems. The use of the model in reactor design is illustrated in one of the homework problems at the end of this module.

**LAMINAR FLOW REACTOR**

When the Reynolds number in a homogeneous tubular reactor is less than a certain critical value, the flow follows distinct streamlines, and a velocity profile is maintained across the flow channel cross section. For a Newtonian fluid flowing in a channel with a circular cross section, the velocity profile is parabolic; \( u(r) \) equals 0 at the tube wall and is at its maximum at the tube axis. A tracer injected into a fluid in laminar flow distributes itself in accordance with the flow streamlines; a slug of tracer injected proportionally to local flow rate across the flow channel cross section eventually appears as shown in Figure 22. Eventually, radial and axial diffusion of the tracer distort the shape of this figure, but as long as this does not occur, the impulse response appears as that shown in Figure 23. If \( L \) is the distance from the injection point to the detection point, and \( u_{\text{max}} \) is the maximum (centerline) velocity, then the *breakthrough time* \( t_b \) (the time when tracer first appears at the detection point) equals \( L/u_{\text{max}} \).

Analysis of laminar flow reactors is more complex than one might imagine. The precise shape of the impulse response depends not only on the velocity profile, but also on how the tracer is injected and detected, so that interpretation of the response is generally uncertain. Moreover, if the reactor is too short, entrance and exit effects dominate the reactor performance, while if it is too long, diffusion leads to deviations from the simple streamline flow behavior, which is the basis of the laminar flow reactor model.

See Reference (2) for further discussion of laminar flow reactors and reactor modeling in general.

**NOMENCLATURE**

\[ C_A \quad \text{reactant concentration} \]
\[ C_A^f \quad \text{reactant concentration in the outflow} \]
\[ C_{A_0} = \text{reactant concentration in the feed} \]
\[ c = \text{tracer concentration in the outflow} \]
\[ D_v = \text{axial dispersion coefficient} \]
\[ k = \text{reaction rate constant} \]
\[ L = \text{reactor length} \]
\[ m_i = \text{mass of tracer injected in an impulse injection} \]
\[ N = \text{number of tanks (CSTR's) in series} \]
\[ q = \text{volumetric flow rate} \]
\[ R = \text{system response proportional to exit tracer concentration} \]
\[ R_u = \text{initial system response} \]
\[ r = \text{intrinsic rate of reaction} \]
\[ -r_A = \text{rate of disappearance of reactant } A \]
\[ t = \text{time} \]
\[ \bar{t} = \text{mean residence time} \]
\[ u(r) = \text{velocity profile in laminar flow as function of radial position} \]
\[ u_{\text{max}} = \text{maximum velocity} \]
\[ V = \text{volume of the reactor} \]
\[ V_s = \text{active volume} \]
\[ V_v = \text{stagnant volume} \]
\[ x_A = \text{fractional conversion of reactant } A \]
\[ \psi = \text{recycle ratio} \]

**LITERATURE CITED**


**STUDY PROBLEMS**

1. What phenomena are responsible for deviations from ideal plug flow in a tubular reactor? Why must approximate models be used to analyze reactors in which these deviations occur?

2. How would you determine from the results of an impulse response measurement whether a reactor can be treated as an ideal PFR, a perfect mixer, or neither?

3. How would you determine the mean residence time in an ideal PFR from a measured impulse response? How would you determine \( \bar{t} \) for a perfect mixer?

4. State several causes for the existence of stagnant regions in flow reactors. How are such reactors modeled?

5. A CSTR containing a stagnant region is to be modeled as a perfect mixer with dead volume. How could the active volume fraction \( (V_{\text{active}}/V_{\text{total}}) \) be determined from a measured impulse response?

6. Suppose the conversion achieved in the reactor of the previous question is not equal to the conversion predicted by the model. What might be responsible for the discrepancy?

7. What are some conditions that lead to channelling in a chemical reactor? How can such a reactor be modeled?

8. Suppose an impulse response consists of two distinct peaks. How would you model the reactor? What is the significance of the ratio of the areas under each peak?

9. What is meant by the term axial dispersion? What models may be used to represent a reactor in which dispersion is observed?

10. Match each of the impulse responses in Figure 24 with the models you would use to represent the reactors in which they were obtained.
   a) Ideal plug flow
   b) Perfect mixer
   c) Laminar flow
   d) Dispersion model
   e) Ideal plug flow with bypass
   f) Ideal plug flow with dead volume
   g) Ideal plug flow with recycle
   h) Perfect mixer with dead volume

**HOMEWORK PROBLEMS**

1. An impulse response test is carried out on a continuous stirred tank reactor using a radiotracer. The throughput rate is 5.0 L/s. The response plotted on semilog paper appears in Figure 25.
   a) Is it appropriate to treat the tank as a perfect mixer? Explain.
   b) Calculate the mean residence time in the tank.
   c) If a mean residence time of one minute is desired, what volumetric throughput rate is required?

2. A 45-liter CSTR is subjected to an impulse response

   ![Figure 24](image1)
   ![Figure 25](image2)
test. The feed rate is 5 liters/second. The following response is obtained.

<table>
<thead>
<tr>
<th>t (s)</th>
<th>R (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>49.0</td>
</tr>
<tr>
<td>10</td>
<td>24.0</td>
</tr>
<tr>
<td>15</td>
<td>11.7</td>
</tr>
<tr>
<td>20</td>
<td>5.7</td>
</tr>
<tr>
<td>25</td>
<td>3.2</td>
</tr>
<tr>
<td>30</td>
<td>2.0</td>
</tr>
<tr>
<td>35</td>
<td>1.6</td>
</tr>
</tbody>
</table>

a) Use a semilog plot of the data to develop a two-region model for the tank. (See Example 1). Determine the volume associated with each region
b) Suppose a chemical reaction \( A \rightarrow B \) with a rate law

\[-r_A \text{ (mol/L} \cdot \text{s}) = 0.50C_A\]

is to be carried out in the reactor, with a feed rate of 5 L/s. Calculate: i) the fractional conversion of \( A \) which would be predicted assuming that the reactor behaves like a perfect mixer; ii) the conversion which would actually be achieved, based on the results of the impulse response test.

3. An experimental reactor (Figure 26) has a double pipe configuration: the feed enters and passes through the inner tube, then returns through the outer tube and passes out of the reactor. A liquid-phase, second-order reaction, \( 2A \rightarrow B \), is to be carried out in the reactor, which operates isothermally. The feed contains \( A \) at a concentration 10.0 mol/L, and no \( B \). The mean residence time in the reactor is 2.00 minutes. In a batch run with an initial concentration of 12.5 mol/L, a 50% conversion was obtained in 20 seconds.

a) Calculate the reaction rate constant, and prove that the concentration of \( B \) in the product which should be achieved if the flow unit performs as an ideal plug flow reactor is 4.14 (mol/L).

b) In the first experimental test of the reactor the concentration of \( B \) in the product is found to be 3.43 (mol/L). An impulse response is performed, and a response approximately equal to that shown in Figure 27 is obtained. Use this response to formulate a model for the reactor. Use the model to predict the expected concentration of \( B \) in the product, and compare your result with the experimental value.

c) Suggest an explanation for the observed reactor behavior.

4. Derive Equation 2 for the impulse response of a

**Figure 26.**

![Diagram](image)

5. Suppose a first-order liquid-phase reaction \( A \rightarrow P \) is to be carried out in an isothermal reactor for which a recycle model is appropriate. See Figure 28.

a) Write the design equation for the reactor in terms of the variables shown on the diagram above, and integrate it to prove that

\[ C_{A(r)} = C_{A(i)} \exp \left( \frac{kV}{q(1+\Psi)} \right) \]

Then use a simple material balance about the feed mixing point to derive an expression for \( C_{A(r)} \) in terms of \( C_{A(i)} \), \( q \) and \( \Psi \), and substitute it in the above expression to derive a formula for \( C_{A(r)} \) in terms of \( q \), \( \Psi \), \( k \) and \( V \).

b) Suppose an impulse response test is carried out on the reactor, with the result shown in Figure 29. If the reactor volume is \( V = 200 \) L and the feed rate is \( q = 2 \) (L/s), what is \( \Psi \)?

c) Next suppose \( k = 0.04 \) s\(^{-1}\). Calculate the fractional conversion \( (1 - C_{A(r)}/C_{A(i)}) \) which would be achieved in the reactor, and compare it with the conversion which would be achieved if the same reactor were in ideal plug flow (\( \Psi = 0 \)).

**Figure 27.**

![Graph](image)

**Figure 28.**

![Diagram](image)

**Figure 29.**

![Graph](image)
1. Departures from ideal plug flow are caused by nonuniform velocity profiles, turbulent mixing and molecular diffusion. An exact mathematical representation of a nonideal reactor is a second-order partial differential equation, which is difficult to derive in complete generality and impossible to solve analytically.

2. \[ R \]
   \[ \log R \]
   \[ t \]

   ideal PFR
   perfect mixer
   anything else
   neither

3. (a) (PFR) The time at which the peak emerges equals \( \tau \).
   (b) (PM) The slope of the plot of \( \log R \) vs. \( t \) equals \( \frac{1}{\tau \ln 10} \)

4. Baffles or other obstructions to flow; expansions or contractions in a line; poor mixing in a stirred vessel. Model as an active region plus a dead volume.

5. Say \( q \) = the volumetric throughput rate. A plot of \( \ln qR \) vs \( t \) yields (at low \( t \)) a straight line with slope \( \frac{1}{V_{active} \text{slope}} = \frac{1}{\tau} \) so that \( V_{active} \) can be calculated as \( q / \text{slope} \). Since \( V_{total} \) is presumably known independently, the active volume fraction (and by implication, the stagnant volume fraction) can then be determined.

6. The stagnant region is not truly a dead volume, but rather participates to a lesser extent in the reactive process. A more precise but more complex model would consist of an active zone and a stagnant zone with
mass transfer occurring between them.

7. Imperfect packing in a fixed bed; short circuiting between a tank inlet and outlet. Model as a parallel arrangement of ideal or other reactor types.

8. Two parallel branches. The total flow divides itself between the branches proportionally to the areas under the two peaks.

9. The collective phenomena which lead to axial mixing in a flow unit, viz. radial velocity variations and molecular and turbulent diffusion. Dispersion model and tanks-in-series model.

10. 1b, 2d, 3c, 4f, 5e, 6a, 7h, 8g.
Mixing Effects in Chemical Reactors—III
—Dispersion Model

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OBJECTIVES
At the completion of this module, the student should be able to:
1. Define the concept of axial dispersion.
2. Outline the principal assumptions that underlie the dispersion model, derive the fundamental dispersion model equation, and recognize the conditions of validity and limitations of the model.
3. Estimate an effective axial dispersion coefficient or a Peclet number from a dimensionless correlation, and apply the estimated value to the design or analysis of a tubular flow reactor.
4. For a given reaction system, estimate the conditions under which dispersion effects on conversion may be neglected.

5. Determine the value of the Peclet number from a measured impulse response or from inlet and outlet tracer response peaks by the method of moments.

PREREQUISITE MATHEMATICAL SKILLS
1. Elementary calculus.

PREREQUISITE ENGINEERING AND SCIENCE SKILLS
1. Understand the concept of a reactor model (Module E4.5) and the uses of impulse responses for reactor modeling (Modules E4.4 and E4.5).

Suppose a reaction $A \rightarrow B$ takes place in a plug flow reactor of length $L$ (m) in which fluid velocity is $\bar{u}$ (m/s). Since $A$ is continuously consumed, its concentration decreases steadily with axial position in the reactor, so that a plot of $C_A$ versus $z$ appears as in Figure 1. The existence of a gradient in the concentration of $A$ gives rise to a diffusive motion of $A$ from the reactor inlet to the outlet, which is superimposed on the convective motion of the bulk fluid phase. The performance of the reactor, specifically, the reactant conversion attainable for a given feed and reactor volume, differs from that which would be predicted, assuming ideal plug flow (negligible diffusion), with the magnitude of the difference depending upon the relative rates of diffusion and convection.

To visualize the effect of diffusion on reactor behavior, let us consider what happens to a group of molecules which enter the reactor at a given instant of time. For the sake of discussion, this module will refer to them collectively as tracer molecules, although they could equally well be molecules of any species in the feed to the reactor.

Shortly after injection, the tracer is contained in a relatively small volume. If the reactor is in ideal plug flow, the tracer cloud then moves through the reactor...
without distortion (Figure 2), and emerges in a burst to give the characteristic ideal PFR impulse response, shown in Figure 3, where $Rdi$ is proportional to the fraction of the outflow around time $t$ which consists of tracer molecules. However, if diffusion does take place, the tracer spreads away from the center of the cloud in both the upstream and downstream directions. At various times from injection, the cloud might occupy the positions in the reactor shown in Figure 4. Further suppose that the concentration of tracer molecules in the reactor effluent can be monitored. The measured values would depend on the length of the reactor, the mean fluid velocity, and the rate of diffusion; however, the characteristic shape of a concentration versus time plot is easily envisioned. The response begins when the tracer which has diffused ahead of the centroid of the cloud emerges from the reactor, builds up to a maximum when the bulk of the tracer emerges, and decreases as the trailing portion of the cloud passes the detector. The responses which might be measured for reactors of increasing length are shown in Figure 5.

The spreading in the tracer cloud (or to put it another way, the distribution of tracer molecule residence times in the reactor) is a consequence of molecular diffusion, and also of turbulent mixing, if the Reynolds number exceeds a critical value. In addition, a nonuniform velocity profile causes different portions of the tracer cloud to move at different rates, which also results in a spreading of the measured response at the reactor outlet. The term dispersion is used to denote the combined action of all phenomena—diffusion and nonuniform velocities—which give rise to a distribution of residence times in a reactor. The term backmixing is also used frequently.

There are several questions to be considered regarding the role of dispersion in the design and analysis of chemical reactors:

1. Are there systems where in dispersion has a significant influence on reactor performance?
2. How can one model a reactor in which dispersion is significant?
3. How does the performance of the reactor depend on the model parameters?
4. How can the degree of dispersion in a flow unit be measured?

These questions will be considered in turn in the sections that follow. To keep the analysis from getting overly complex, our attention will be restricted to isothermal reactors in which no expansion occurs (liquid-phase reactions, or gas-phase reactions with no mole changes at constant pressure).

THE DISPERSION MODEL:

The Model Equation

According to Fick's law, the rate of diffusion of a substance $A$ is proportional to the negative of the concentration gradient of $A$. In any tubular reactor, either empty or packed, reactant depletion and nonuniform flow velocity profiles give rise to concentration gradients, and hence diffusion, in both axial and radial directions. In addition, in turbulent flow eddy transport takes place, tending to level out gradients in all directions to an even greater extent than does molecular diffusion.

A reactor model which accurately reflects these phenomena is difficult to derive, and even more difficult to analyze. What is often done instead is to model the reactor making the following two assumptions:

1. The reactor is in plug flow (but not ideal plug flow); radial uniformities are presumed to exist, and the process fluid moves through the reactor at a uniform velocity $\bar{u}$ equal to the mean velocity of the fluid in the reactor being modeled.
2. Dispersion occurs in the axial direction. The extent of the dispersion is sufficient to account for the combined effects of all dispersive phenomena (molecular and turbulent mixing, and nonuniform velocities) in the real reactor. This representation of a flow reactor is termed the dispersed plug flow model, or simply the dispersion model. As has been shown in the literature, it can successfully simulate the behavior of reactors in which complex radial and axial flow and transport patterns exist (3).

To derive the model equation, let us consider Figure 6, a cross section of a dispersed plug flow reactor at steady-state. Suppose that the mean fluid velocity is $\bar{u}$(cm/s) (in a packed bed reactor, $\bar{u}$ is the superficial
velocity), and that $D_e \text{ (cm}^2/\text{s})$ is the constant of proportionality between the dispersive flux of a reactant $A$ and the negative gradient of $A$ in the $z$ direction $(-dC_A/dz)$. The rate at which $A$ traverses the cross section is the sum of the rate at which it is carried through by the convective (bulk) flow of the fluid, plus the rate at which it passes through by dispersion:

$$J_{total} = \bar{u} S C_A - D_e S \frac{dC_A}{dz}$$

The reactor may be considered to be in ideal plug flow to the extent that the second term is negligible relative to the first.

Let us further suppose that $A$ is involved as a reactant, and that the rate at which it reacts is $-r_A$ (mol/cm$^3 \cdot$ s). The steady-state material balance on $A$ in the reactor may be derived by considering a differential element from $z$ to $z + \Delta z$. See Figure 7. The balance takes the form $\text{input} = \text{output} + \text{consumption}$, where the input term is the rate at which $A$ enters the element at $z$ by convection and dispersion, the output term is the rate of passage of $A$ through the cross section at $z + \Delta z$, and the consumption term is the volumetric rate of consumption ($-r_A$) times the volume of the differential element ($S \Delta z$). If the input and output terms are expressed by Equation 1, the result is:

$$\bar{u} S C_A|_z - D_e S \frac{dC_A}{dz}|_z$$

and substitute $LZ$ for $z$ and $C_{A0}$ for $C_A$ in Equation 4, the result may be written as

$$\frac{1}{N \rho_e} \frac{d^2 C}{dz^2} - \frac{dC}{dz} - \frac{N \rho_s}{L} (C^* - 0) = 0$$

where the dimensionless group

$$N_{pe} = \frac{\bar{u} L}{D_e} \frac{(L / \bar{u})}{(L / \bar{u})}$$

is the Peclet number, which represents the ratio of characteristic dispersion time to characteristic convection time (residence time).

The Damköhler number, which represents the ratio of the characteristic convection time (residence time) and characteristic process (reaction) time.

The proper boundary conditions discussed at length in Reference (2) for the reactor at steady state require continuity of flux at the entrance and exit:

$$Z = 0 \quad C \frac{dC}{dZ} = 1$$

The final result is obtained by letting $\Delta z$ approach zero:

$$\bar{u} \frac{dC_A}{dz} = D_e \frac{d^2 C_A}{dz^2} + r_A$$

This is the axial dispersion model equation. Once two boundary conditions are specified and a rate law is substituted for $r_A$, the equation can be solved, analytically or numerically, for $C_A(z)$; the result can in turn be used to determine the reactor length and hence the mean residence time $\bar{u} L/z$ needed to achieve a specified conversion. Here $\epsilon$ is the fraction of the reactor volume occupied by the flowing fluid, i.e., $\epsilon = 1$ for empty tubes and $\epsilon = \text{bed porosity}$ for packed bed reactors.

A number of complexities are associated with the choice of boundary conditions for Equation 4, which center about the question of whether or not diffusion of $A$ across the reactor boundaries takes place. These problems will not be considered here, except to note that the closer the reactor is to ideal plug flow (i.e., the lower the value of $D_e$) the less difference this question makes and the more reliable is the model. For a more complete discussion, see Reference (2).

**Dimensional Analysis of the Dispersion Model**

It is often useful to write a model equation such as Equation 4 in terms of dimensionless variables. Let us define $Z = z/L$ and $C = C_A / C_{A0}$. If one assumes an nth-order rate law,

$$r_A = kC_A^n$$

and substitute $LZ$ for $z$ and $C_{A0}$ for $C_A$ in Equation 4, the result may be written as:

$$N_{pe} \frac{d^2 C}{dz^2} - \frac{dC}{dz} - N_{pe} (C^* - 1) = 0$$

where the dimensionless group

$$N_{pe} = \frac{\bar{u} L}{D_e} \frac{(L / \bar{u})}{(L / \bar{u})}$$

is the Peclet number, which represents the ratio of characteristic dispersion time to characteristic convection time (residence time).

$$N_{pe} = \frac{kC_{A0}^{n-1} L / \bar{u}}{N_{pe}} (C^* - 1)$$

is the Damköhler number, which represents the ratio of the characteristic convection time (residence time) and characteristic process (reaction) time.
\[ Z = 1 \quad \frac{d C}{d Z} = 0 \]  

Equations 5, 5a and 5b complete the statement of the problem.

The degree to which axial dispersion influences the performance of a chemical reactor is determined by the value of the Peclet number. A high value of \( N_p \) corresponds to a slightly dispersed reactor, with \( N_p \rightarrow \infty (D_e \rightarrow 0) \), signifying ideal plug flow. Similarly, a low value of \( N_p \) represents a high degree of backmixing; in the limit as \( N_p = 0 \), backmixing is in effect complete—the concentration of \( A \) is uniform throughout the reaction volume, and the reactor functions as a perfect mixer. Although the validity of the dispersion model depends to a great extent on the process (for a reactor, on the value of the Damkohler number) it may be stated as a rule of thumb that the dispersion model may be used with confidence as long as \( N_p \) is greater than 20, and should be used with increasing caution as the Peclet number falls below this value.

This dispersion model has been found especially useful in modeling the behavior of packed bed reactors. A dimensionless group which frequently occurs in this context is the Bodenstein number

\[ N_{Be} = \frac{\bar{u}d_p}{\epsilon D_e} \]  

where \( d_p \) is the mean particle diameter of the packing and \( \epsilon \) is the void fraction (porosity) of the bed. The inverse of the Bodenstein number, \( \epsilon / \bar{u} D_e \), is sometimes called the intensity of dispersion*. Here \( D_e \) is the dispersion coefficient based on actual cross sectional area available for fluid transport.

**Analysis of Dispersed Plug Flow Reactors**

To predict the conversion which will be achieved in a dispersed plug flow reactor for a reaction with known kinetics, one must integrate Equation 4 or 5, substituting values of the superficial velocity \( \bar{u} \) and the effective axial dispersion coefficient \( D_e \). The velocity can be easily determined as the volumetric flow rate of the reaction mixture divided by the cross-sectional area of the empty reactor; the problem is to determine \( D_e \).

As will be shown in a later section, axial dispersion coefficients (or equivalently, Peclet numbers) can be determined from tracer response measurements. The results of many such measurements have been used to derive correlations which may be used to estimate dispersion coefficients from known reactor geometric variables and reaction mixture properties. In the remainder of this section, two such correlations will be presented. The module will illustrate how to use them, and show how the performance of a dispersed plug flow reactor can be predicted once the value of \( D_e \) has been estimated.

**Correlations for Dispersion Coefficients**

Wen and Fan [Reference (2), Figures 5-15 through 5-22] summarize correlations for straight pipes, fixed and fluidized beds, and bubble towers. The correlations involve the following dimensionless groups:

\[ \frac{\bar{u} d_p}{\nu} \text{ Reynolds number (empty tubes)} = d_p \bar{u}/\nu \text{ Particle Reynolds number (packed beds)} \]

\[ N_{Be} = \frac{\nu}{D_{mol}} \text{ Schmidt number} \]

where \( d \) (cm) is the flow channel diameter for an empty tube, \( d_p \) is the mean particle diameter for packed beds, \( \nu (cm^2/s) \) is the kinematic viscosity of the fluid (viscosity/density), and \( D_{mol} \) is the molecular diffusivity of the reactant (or tracer) in the fluid \( (D_{mol} \approx 10^{-5} \text{ cm}^2/s \text{ for liquids}, 1 \text{ cm}^2/s \text{ for gases}) \). If the viscosity and density of the reaction mixture, the flow channel diameter, and void fraction of the bed, and the superficial fluid velocity are known, one can calculate the Reynolds number, estimate the intensity of dispersion from the appropriate correlation, and use the resulting value to estimate the effective dispersion coefficient \( D_e \) or \( D' \).

Figures 8 and 9 present two such correlations, the first for fluids flowing through empty pipes and the

*Unfortunately the terminology regarding these dimensionless groups is not universally accepted, and you should be aware that other conventions are commonly used. The term "Bodenstein number" is sometimes used to denote the Peclet number as defined by Equation 6, and what we have called the Bodenstein number is also called the "Peclet number based on particle diameter."
second for flow in packed beds. Their use will be illustrated in the next section.

**Effect of Dispersion on Reactor Performance**

The performance of an isothermal dispersed plug flow reactor can be analyzed by substituting a rate law into Equation 4 or 5 and integrating the resulting equation (analytically for a first-order reaction, otherwise numerically) to determine the reactant concentration (or fractional conversion) versus axial position.

The qualitative effect of dispersion can be inferred by noting that, as the dispersion coefficient $D_e$ varies from 0 to $\infty$, the reactor behavior changes from ideal plug flow to perfect mixing. Recall that for a single nth-order reaction at constant temperature, the conversion obtained in a perfect mixer is always less than that obtained in an ideal PFR with the same space time. One might then guess that as the rate of dispersion increases (or equivalently, as $D_e$ increases), conversion decreases. This is in fact the case.

Figure 10 shows the results of solving Equation 4 for a first-order reaction: the abscissa is $(C_{A,\text{inlet}}/C_{A,\text{inlet}}) (1 - x_A)$, and the ordinate is the ratio of the dispersed plug flow reactor volume to the volume of an ideal PFR which would be required to achieve the same conversion. A similar graph for a second-order reaction is given by Levenspiel in Reference (1), chapter 9, Figure 22.

![Figure 9. Correlation of Bodenstein number with Reynolds and Schmidt numbers for flow of gases through fixed beds (2).](image)

![Figure 10. Ratio of dispersed plug flow reactor volume to ideal plug flow reactor volume versus 1-fractional conversion for first-order reaction $A \rightarrow$ products, assuming negligible expansion (1).](image)
value for ideal plug flow \((D_p = 0)\) to a maximum for a perfect mixer \((D_p = \infty)\).

Figure 10 can be used in several ways. Suppose a first-order reaction with a known rate constant \(k\), is being carried out in a continuous isothermal tubular reactor. If the throughput \(q\) (m\(^3\)/s) and desired conversion \(X_A\) are specified then:

1. Calculate the required ideal plug flow reactor volume as

\[
V_p = \frac{q}{k} \ln (1 - X_A) = \frac{q}{K} \ln \left( \frac{1}{1 - X_A} \right)
\]  

(Be sure you know where this formula comes from.)

2. Specify a flow channel (or packing particle) diameter, calculate \(S\), the flow channel cross section, and determine the superficial velocity \(\bar{u} = q/S\) and the ideal plug flow reactor length \(L_p = V_p / S\).

3. Calculate the Reynolds number \(N_{Re} = \bar{u}D_p / \nu\) (or \(d_p \bar{u} / \nu\) for a packed bed), then use the appropriate correlation (e.g., Figure 8 for an empty tube) to estimate the dispersion intensity \(D_{p}\bar{u}d\bar{u}\). (If the flow is laminar, one must also determine the Schmidt number to use the correlation.) Next, from the value of \(D_{p}\bar{u}d\bar{u}\) and the known tube diameter, calculate the ratio \(\bar{u} / D_p\), and finally calculate the inverse Pecllet number \(D_{p}\bar{u}d\bar{p}\), using the value of \(L\) calculated assuming ideal plug flow.

4. Locate the specified conversion on the abscissa of Figure 10. Then

a) To estimate the reactor volume required to achieve the same conversion, move up vertically to the curve corresponding to the calculated inverse Pecllet number, read \(V/V_p\) on the ordinate, and calculate \(V\) from the known value of \(V_p\). (One can refine the calculation by recalculating \(D_{p}\bar{u}d\bar{u}\) with the new value of \(V\), and repeating until the initial and final values of \(V\) agree.)

b) If, instead, one wished to calculate the final conversion which will be achieved in the reactor of length \(L_p\), move up the constant \(k\?d\bar{u}\) to the curve corresponding to the calculated value of \(D_{p}\bar{u}d\bar{p}\), and read the abscissa value (Question: why is \(k\?d\bar{u}\) constant in this calculation?).

For a first-order reaction, an analytical solution of the axial dispersion equation is available (2). It is instructive to compare the results obtained using Figure 10 with this solution. However, graphical representations similar to Figure 10 are useful for reaction orders other than one for which analytical solutions are not available.

### Criteria for Neglecting Dispersion Effects

Although the dispersion model is a relatively simple approximation to the behavior of a real reactor, it is still much more cumbersome to use than the ideal plug flow model. It is therefore important for the design engineer to be able to predict whether or not dispersion effects must be taken into account in assessing reactor performance. Criteria can be developed by applying perturbation theory to Equation 5. See, for instance, References (4) and (5). Only the pertinent results will be presented in this section.

Suppose one is carrying out an \(n\)-order reaction \(\ce{A \rightarrow B}\) in a continuous reactor of length \(L\). Several questions may be asked:

a) Given rate law parameters \((k_p, n, \text{and } n)\) and a desired fractional conversion \(X_A\), what condition guarantees that the required volume of an ideal PFR and that which would be calculated (taking dispersion into account) will be within \(p^{10}\%\) of each other?

**Conditions**

\[
N_{Re} \geq \frac{100}{p} \frac{n}{N_{Re}} \ln \left( \frac{1}{1 - X_A} \right) \quad \text{(any reactor)}
\]

\[
\frac{L}{d_p} \geq \frac{100}{p} \frac{n}{N_{Re}} \ln \left( \frac{1}{1 - X_A} \right) \quad \text{(packed bed)}
\]

**Procedure:**

Use a dimensionless correlation to estimate the value of \(N_{Re}\) or \(N_{Re}\) from the design variables; choose a value of \(p (5\% \text{, for example, or } 1\% \text{ if a closer tolerance is required})\), and see if the condition of Equation 10 or 11 is satisfied. If it is, use the ideal plug flow model as the basis of the design.

b) Given a set of reactor parameters (including length), what condition guarantees that the fractional conversion predicted assuming ideal plug flow and that which would be predicted taking dispersion into account will be within \(p^{10}\%\) of each other?

**Conditions:**

\[
N_{Re} \geq \frac{100}{p} (N_{Re})^2 \quad \text{and} \quad n = 1
\]

\[
\frac{L}{d_p} \geq \frac{100}{p} \frac{(N_{Re})^2}{N_{Re}} \quad \text{and} \quad n = 1
\]

\[
\frac{L}{d_p} \geq \frac{100}{p} \frac{n}{N_{Re}} \frac{N_{Re}}{\left[1 + (n-1)N_{Re}\right]} \quad \text{and} \quad n = 1
\]

\[
\frac{L}{d_p} \geq \frac{100}{p} \frac{n}{N_{Re}} \frac{N_{Re}}{\left[1 + (n-1)N_{Re}\right]} \quad \text{and} \quad n = 1
\]

Note in the case of packed bed reactor, the reaction rate constant in the above formulas is based per unit reactor volume.

**Example 1:**

A second-order gas-phase reaction \(\ce{A \rightarrow B}\) takes place in an isothermal packed bed reactor. The particle Reynolds number is greater than 50, and the length of the reactor...
determined for desired conversion assuming ideal plug flow is 7.2 meters. The mean particle diameter of the packing is 1 cm. The Schmidt number of the gas is close to 1. The Damkohler number is evaluated and is found to equal 29. Would the conversion actually achieved be within 1% of the specified value?

**Solution:**

Use Equation 15.

\[ L/d_p = (720 \text{ cm})/(1 \text{ cm}) = 720 \]

From Figure 9, for a Reynolds number of 50 and a Schmidt number of 1, set \( N_{Be} = 2 \). The right-hand side of Equation 15 is then determined to be

\[ \frac{100}{1} \left( \frac{2}{1} \right) \left[ \frac{2.9}{2(1+2.9)} \right] \ln (1+2.9) = 101 \]

Since 720 > 101, according to Equation 15 one can use the ideal plug flow design calculation with confidence.

The next example illustrates the design of a reactor under conditions when dispersion cannot be neglected.

**Example 2:**

A liquid-phase reaction \( A \rightarrow B \) is to be carried out in an isothermal tubular reactor. The rate law for the reaction at the proposed operating temperature is

\[ r_A = 0.40 \, \text{cm}^3 / \text{s} \]

A pipe with an 8 cm inner diameter is to be used, and a 99% conversion is desired. The feed is pure \( A \), and the throughput rate is 0.24 L/s. Calculate the conversion which will be achieved in the reactor, taking axial dispersion into account. The fluid properties of the reaction mixture may be taken to be those of pure water.

**Solution:**

If the reactor were in ideal plug flow, the required volume would be:

\[ V_p = \frac{q}{k} \ln (1 - X_A) \]

\[ = -0.24 \text{ L/s} / 0.40 \text{ s}^{-1} \ln (1 - 0.99) = 2.76 \text{ L} \]

and its length would be

\[ L_p = \frac{2.76 \times 10^3 \text{ cm}^3}{(\Pi \times 4^2) \text{ cm}^2} = 54.9 \text{ cm} \approx 55 \text{ cm} \]

The mean velocity of the reaction mixture is

\[ \bar{u} = \frac{q/S}{(\Pi \times 4^2) \text{ cm}^2} \]

\[ \approx 4.8 \text{ cm/s} \]

The density of the fluid is 1.0 (g/cm³), and its viscosity is 0.010 (g/cm-s), so that its kinematic viscosity is

\[ \nu = \frac{0.010}{1} \text{ (g/cm·s)} = 0.010 \text{ (cm²/s)} \]

The Reynolds number is

\[ N_Re = \frac{d \bar{u}}{\nu} = \frac{(8 \text{ cm})(4.8 \text{ cm/s})}{0.01 \text{ cm²/s}} = 3840 \]

The flow is thus turbulent, and there is no need to calculate the Schmidt number. From Figure 8, for a Reynolds number of 3840

\[ D_e / \bar{u} \leq 2 \]

\[ \frac{D_e}{\bar{u}} \leq \frac{D_e}{\bar{u}} \bar{u} \leq \frac{8}{2} \frac{1}{55} = 0.29 \]

The Damkohler number for this reactor is

\[ N_{Da} = \frac{k C_A^m}{\bar{u}} = \frac{(0.40)(1)(55)}{4.8} = 4.58 \]

Let us see if the conversion obtained in the reactor is within 1% of the ideal PFR value of 0.99. The right-hand side of Equation 12 is

\[ \frac{100}{1} (4.58)^2 = 2098 \]

while the Peclet number is 1/0.29 = 3.4. The condition of Equation 12 is thus not satisfied, and dispersion should accordingly be taken into account in the design.

The point \( 1 - X_A = 0.01 \) is located on the abscissa of Figure 10 (it is the origin of the graph). A line of constant \( k \bar{u} \) is followed until the point corresponding to \( D_e / \bar{u} \leq 0.29 \) is reached, at which point, \( 1 - X_A = 0.06 \). The effect of the dispersion is therefore to lower the achievable conversion from the design value of 99% to 94%.

One can also estimate the volume required to achieve the 99% conversion for the same throughput rate. Proceeding vertically from the 99% conversion point to the curve for \( D_e / \bar{u} = 0.29 \), estimate \( V/V_p = L/L_p \approx 2.0 \), so that to a first approximation, a length of roughly (2.0)(55.9) = 110 cm is required to achieve the desired conversion, when dispersion is taken into account. (The estimate can be refined by recalculating \( D_e / \bar{u} \) using the new value of \( L \), reading \( V/V_p = L/L_p \) again from Figure 10, and iterating until two successive values of \( L \) agree.)

**MEASUREMENT OF AXIAL DISPERSION COEFFICIENTS**

Suppose a tracer impulse is injected at the inlet of a dispersed plug flow reactor, and the response is monitored at the outlet. The shape of the response depends on the relative magnitudes of the rates of convection and dispersion: if dispersion is much slower than convection, the reactor behaves as though it were in ideal plug flow, while if dispersion is very rapid compared to convection, the reactor approaches a perfect mixer in its behavior.

The Peclet number \( N_{Pe} = \bar{u}L/D_e \) (which can be thought of as a ratio of the rate of convection to the rate of dispersion) provides a measure of the extent of
deviation from ideal flow conditions: \( N_{Pr} \to \infty \) corresponds to ideal plug flow, and \( N_{Pr} = 0 \) represents perfect mixing. Representative impulse responses corresponding to various degrees of dispersion, and several values of \( N_{Pr} \), are shown in Figure 11a, b, c and d. \( R(t) \) is a property of the outflow which is directly proportional to tracer concentration and which is monitored as the response of the system to an impulse tracer injection in the inflow.

There are several statistical techniques which can be used to extract the value of \( D_e \) from a tracer response. One such technique is the method of moments. Derivations of the formulas to be given, and discussions of alternative estimation methods, may be found in Reference (2).

If a tracer impulse is injected at a reactor inlet and \( R(t) \) is the measured response at the outlet, the first step in implementing the method of moments is to calculate the following quantities by numerical integration:

\[
\mu = \frac{\int_0^\infty tR(t)dt}{\int_0^\infty R(t)dt}
\]

is the mean or centroid of \( R(t) \).

\[
\sigma^2 = \frac{\int_0^\infty (t-\mu)^2 R(t)dt}{\int_0^\infty R(t)dt}
\]

is the variance of \( R(t) \). The mean \( \mu \) is the average value of the response time \( t \), and the variance is a measure of the spread of the response peak about the mean; a low value of \( \sigma^2 \) corresponds to a narrow peak, and conversely.

If the peak is symmetrical (like those in Figure 12), the mean \( \mu \) coincides with the time at which the response is a maximum, and in general, corresponds to the mean residence time in the system (see Module 4.4). The value of \( \sigma^2 \) depends very strongly on the degree of dispersion in the system; the higher the degree of dispersion, the more the response curve spreads and hence, the greater the value of \( \sigma^2 \).

It can be shown (3) that if the degree of dispersion is not too great,

\[
\sigma^2 \approx \frac{2}{N_{Pr}} \frac{2D_e}{uL}
\]

(18)

The criterion for the validity of Equation 18 is \( N_{Pr} \gg 1 \); a rough rule of thumb is \( N_{Pr} > 10 \). If this condition is not satisfied, the correct formula depends on the boundary conditions at the inlet and outlet, and the validity of the dispersion model itself becomes questionable. [The formulas applicable for different boundary conditions are given by Reference (1) and (2).] A procedure for determining \( D_e \) is thus as follows:

1. Measure the outlet response \( R(t) \) to a tracer impulse injected at the inlet.
2. Calculate the mean, \( \mu \), and the variance, \( \sigma^2 \), according to Equations 16 and 17 by numerical integration.
3. Estimate the Peclet number using Equation 18 as:

\[
N_{Pr} = 2\mu^2/\sigma^2
\]

(19)

If the value is 10 or greater, accept it; if not, either use a refinement of the theory which takes into account the boundary conditions at the outlet, or use a different model altogether.

4. Determine the mean (superficial) fluid velocity \( \bar{u} \) as the volumetric flow rate divided by the flow channel cross section, or if both are not known, as

\[
\bar{u} = \bar{e}L/\mu
\]

(20)

5. Estimate \( D_e \) from the definition of the Peclet number as

\[
D_e = \bar{u}L/N_{Pr}
\]

(21)

Example 3:
An impulse response measurement is carried out on a tubular reactor 4 meters long. The pipe inner

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diameter is 10 cm, and the volumetric flow rate is 0.63 L/s. The response appears in Figure 13, and is corrected by subtracting the constant background signal \( R_c \); the mean and variance of the corrected signal are calculated using Simpson's rule (using a computer program such as the one available for Module E4.4), with the following results:

\[
\mu = \int_0^\infty t R_c(t) dt = 50 \text{ s}
\]

\[
\sigma^2 = \int_0^\infty (t - \mu)^2 R_c(t) dt = 62.5 \text{ s}^2
\]

From Equation 19, the Peclet number is estimated to be

\[
N_P = \frac{2\mu^2}{\sigma^2} = \frac{2(50)^2}{62.5} = 80
\]

Since this is greater than 10, the dispersion model and the estimated value of the Peclet number can be used with a reasonable degree of confidence. The mean velocity is calculated as

\[
\bar{u} = \frac{Q}{A} = \frac{0.63 \times 1000}{\pi(0.05)^2} = 8.02 \text{ cm/s}
\]

and from Equation 21

\[
D_e = \frac{\bar{u}L}{N_P} = \frac{(8.02 \text{ cm/s})(400 \text{ cm})}{80} = 40.1 \text{ cm}^2/\text{s}
\]

**Determination of \( D_e \) — Two Peak Method**

It is not always possible to inject a tracer in a time period short enough to be considered instantaneous compared to the residence time of the fluid in the system under investigation (recall that this was the condition for the injection to be treated as a perfect impulse). Fortunately, the analysis outlined in the preceding section can still be performed with relatively few additional calculations, if a tracer pulse (not necessarily an impulse) is injected at a point upstream of the inlet of the system to be modeled, and the responses at the inlet and outlet are measured.

The dispersion coefficient can be calculated from the means and variances of the inlet and outlet response curves. In Figure 14, let \( r \) be the time from the beginning of the injection. First calculate:

\[
\mu_1 = \int_0^\infty t R_1(t) dt \quad \text{and} \quad \mu_2 = \int_0^\infty t R_2(t) dt
\]

\[
\sigma_1^2 = \int_0^\infty (t - \mu_1)^2 R_1(t) dt, \quad \sigma_2^2 = \int_0^\infty (t - \mu_2)^2 R_2(t) dt
\]

In terms of these moments, the mean and variance of the system impulse response are

\[
\mu = \mu_2 - \mu_1 \quad (23)
\]

\[
\sigma^2 = \sigma_2^2 - \sigma_1^2 \quad (24)
\]

Thus, one can calculate the desired impulse response moments while avoiding the need for a perfect impulse injection or anything close to it. Once \( \mu \) and \( \sigma^2 \) are known, \( D_e \) may be calculated from Equation 18, as before.

**NOMENCLATURE**

- \( C \) = dimensionless reactant concentration
- \( C_A \) = reactant concentration
- \( C_{A_p} \) = reactant concentration in the feed
- \( D_e \) = axial dispersion coefficient based on total cross-sectional area
- \( D_e' \) = axial dispersion coefficient based on cross-sectional area available for fluid flow
- \( D_{mol} \) = molecular diffusivity
- \( d \) = tube or vessel diameter
- \( d_p \) = particle diameter
- \( J_{total} \) = total flux (convection + dispersion)
- \( k \) = reaction rate constant
- \( L \) = reactor length (calculated by the axial dispersion model)
- \( L_f \) = reactor length (calculated by the ideal plug flow model)
- \( N_{Bo} = \bar{u}d_e/\varepsilon D_e' \) = Bodenstein number
- \( N_{Da} = kC_A^2n^3L/\bar{u} \) = Damkohler number
- \( N_{Pe} = \bar{u}L/D_e \) = Peclet number
- \( N_{Re} = \varepsilon (d_e\bar{u})/\nu \) = Reynolds number
- \( N_{Sc} = \nu/D_{mol} \) = Schmidt number
- \( n \) = reaction order
- \( p \) = percent deviation from ideal plug flow reactor solution
- \( q \) = volumetric flow rate
\[ R = \text{system response to impulse injection} \]
\[ -r_A = \text{rate of reaction (disappearance) for reactant } A \]
\[ S = \text{cross-sectional area of the reactor} \]
\[ t = \text{time} \]
\[ \bar{t} = \text{mean residence time} \]
\[ \bar{u} = \text{mean velocity} \]
\[ V = \text{reactor volume} \]
\[ V_p = \text{volume of an ideal plug flow reactor} \]
\[ x_p = \text{fractional conversion of reactant } A \]
\[ Z = z/L = \text{dimensionless axial position in the reactor} \]
\[ z = \text{axial position in the reactor} \]
\[ \varepsilon = \text{porosity (external voidage) of packed beds} \]
\[ \varepsilon_k = \text{gas holdup (fraction of reactor volume occupied by gas)} \]
\[ \mu = \text{first moment of impulse response (or viscosity)} \]
\[ \nu = \text{kinematic viscosity} \]
\[ \sigma^2 = \text{variance of impulse response} \]

6. A first-order reaction is carried out in a tubular reactor. By inspection of Figure 10, indicate whether the following statements are true or false:
(a) As the Peclet number goes from 0 to \( \infty \), the performance of a flow reactor varies from that of an ideal CSTR to that of an ideal PFR.
(b) For a given flow rate, the assumption of ideal plug flow is more likely to be valid for a long reactor than for a short one.
(c) As the effective dispersion coefficient increases from 0 to infinity for a given flow rate and reactor length, the conversion in the reactor goes from its ideal plug flow value to 0.

7. Would you use an ideal plug flow model, a perfect mixer model, or neither, to simulate a reactor for which \( N_{pe} = 1.0 \times 10^{-3} \)?
(a) 1.0 \times 10^{-3}; (b) 1.0 \times 10^6; (c) 1.0 \times 10^9?

8. Sketch impulse responses corresponding to a) slightly dispersed plug flow; b) moderately dispersed plug flow; c) highly dispersed plug flow.

9. What are the physical significances of the mean and the variance of an impulse response?

10. How would you calculate the Peclet number for a flow unit from a measured impulse response?

11. How would you calculate the Peclet number for a flow unit from measured tracer response peaks at the inlet and outlet of the unit?

12. What is the advantage of the two-peak method?

**LITERATURE CITED**


**STUDY PROBLEMS**

1. What is meant by the term axial dispersion?

2. How would the dispersion model equation, Equation 4, simplify for an ideal plug flow reactor?

3. What assumptions underlie the dispersion model? Under what conditions is this model most likely to provide an accurate representation of a flow reactor?

4. Suppose you have designed a tubular reactor. Outline how you would obtain an estimate of the value of the effective dispersion coefficient in the unit from the known flow rate of the reaction mixture, physical properties of the fluid, and the tube dimensions.

5. Once you have gone through the exercise of the previous example and estimated \( D_e \), how would you estimate the conversion for a first-order reaction which would be achieved if the reactor had been designed to achieve a 95\% conversion, assuming ideal plug flow?

**HOMEWORK PROBLEMS**

1. A reaction mixture flows through a 4 cm inner diameter tubular reactor at a rate of 25 cm$^3$/s. The concentration of a reactant varies with axial position in the reactor according to the formula
\[ C_d (\text{mol/cm}^3) = 3.00 \exp (-0.200z) \]
where \( z \) (cm) is the distance from the reactor inlet. The axial dispersion coefficient of the reactant is 0.02 cm$^2$/s.
(a) Calculate the flux of the reactant, J(mol/s), through the cross section at \( z = 10 \) cm.
(b) What is the predominant mode of transport—axial convection or dispersion?

2. An 8 cm ID tubular reactor has been designed to achieve a 98\% conversion of the reactant in a first-order reaction. The specified reactor length is 110 cm. In a batch run at the specified reaction temperature, the reactant half-life was found to be 4.6 seconds. The kinematic viscosity of the reaction mixture is 0.012 cm$^2$/s.
(a) What throughput rate (cm$^3$/s) is the reactor designed to accommodate?
(b) Use Figures 8 and 10 to estimate the percentage
difference between the design conversion and the conversion which will actually be achieved. (c) Comment on the applicability of the dispersion model for this reactor.

3. An impulse response test is performed on an empty tubular reactor. The flow rate through the reactor is 8 L/s, and the reactor inner diameter is 10 cm. The response at the outlet can be approximated as in Figure 15.

a) Estimate the reactor volume and the Peclet number. You may find it helpful to know that for the response shown in the figure

\[ \int_0^\infty (t-5)R(t)dt = 3.65 \text{ s}^3 \]

b) Is the dispersion model appropriate to simulate the reactor? Explain.

c) Suppose a first-order reaction is to be carried out in the reactor and a 95% conversion is specified. Is an ideal plug flow model suitable for the design calculation? Justify your answer.

4. In Figure 16 sulfur dioxide is to be absorbed in an aqueous KOH solution in a packed column. The packed section is 1 meter in diameter. The volumetric flow rate of the gas stream in the absorber is approximately constant at 0.016 m³/s. A pulse of radioactive argon (⁴¹Ar) is injected into the gas feed line, and the responses close to both ends of the packed bed are monitored with externally mounted scintillation detectors 4 meters apart from each other. The responses corrected for background and decay appear as shown in Figure 17. The means and variances of these signals are calculated by numerical integration, with the following results:

\[ \mu_1 = 1.8 \text{ s}, \ \mu_2 = 73.8 \text{ s} \]
\[ \sigma_1^2 = 0.4 \text{ s}^2, \ \sigma_2^2 = 15.3 \text{ s}^2 \]

Use these results to estimate the mean residence time of gas in the packed bed (more precisely, in the portion between the detectors) the gas holdup (the fraction of reactor volume occupied by gas) eg (m³ gas space/m³ total volume), and the effective gas-phase dispersion coefficient \( D_e \) (cm²/s). Comment on the applicability of the dispersion model.
1. The combined action of all phenomena--molecular and turbulent diffusion, and a nonuniform velocity profile--that give rise to a distribution of residence times in a reactor.

2. The second derivative term is deleted. \((D_e = 0)\).

3. All radial nonuniformities and axial mixing phenomena can be represented as plug flow with axial diffusion. The model is most reliable under conditions close to ideal plug flow (slight degree of dispersion).

4. Calculate the Reynolds number, calculate the Schmidt number for laminar flow, look up the Peclet number or the dispersion intensity on a graphical correlation (e.g. Figure 8), calculate \(D_e\) from known \(\bar{U}\) and \(d\).

5. Calculate \(\frac{D_e}{\bar{U}L}\). Find 0.05 on abscissa of Figure 3, move up line of constant \(k_e\) to value of \(\frac{D_e}{\bar{U}L}\), read corresponding value of \(1-x_A\), calculate \(x_A\).

6. (a) true; (b) true; (c) false

7. (a) perfect mixer; (b) neither; (c) ideal PFR

8. 

9. The mean is approximately equal to the mean residence time in the flow unit. The variance is a measure of the degree to which individual residence times are spread about the mean.

10. Calculate \(\mu\) and \(\sigma^2\) by numerical integration; calculate \(Pe = 2\mu^2/\sigma^2\).

11. Calculate the means and variances of both peaks by numerical integration, then \(\mu = \mu_{out} - \mu_{in}\), \(\sigma^2 = \sigma^2_{out} - \sigma^2_{in}\) then \(Pe = 2\mu^2/\sigma^2\).

12. It does not require a perfect impulse injection.
Module E4.7

Mixing Effects in Chemical Reactors—IV
—Residence Time Distributions

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OBJECTIVES
At the completion of this module, the student should be able to
1. Define the residence time density function \( E(t) \) and residence time distribution \( F(t) \).
2. Determine \( E(t) \) and \( F(t) \) from measured tracer impulse and step responses.
3. Calculate the nominal mean residence time in a process unit and the mean of the residence time distribution, and state when the two quantities are equal.
4. Calculate the functions \( E \) and \( F \) in terms of reduced time \( \theta = t/T \).
5. Determine qualitatively the degree of axial mixing, bypassing, and internal recirculation in a process unit, and quantitatively the extent of stagnancy in a unit, from a measured residence time distribution.
6. Determine effective phase volumes in multiphase reactors from tracer responses.

PREREQUISITE MATHEMATICAL SKILLS
1. Calculus.

PREREQUISITE ENGINEERING AND SCIENCE SKILLS
1. Mixing in chemical reactors (Modules E4.4 and E4.5).

The performance of a continuous chemical reactor depends to a great extent on the flow and mixing patterns in the reactor. You have performed design calculations for ideal plug flow reactors and perfect mixers, for example, and you know that they may yield significantly different conversions for a specific reaction rate and a given mean residence time.

The behavior of continuous chemical reactors cannot always be described in terms of either ideal plug flow or perfect mixing. Imperfect mixing in stirred tanks, nonuniform flow velocities in tubular reactors, and diffusion in any direction in which concentrations vary make the exact relationship between feed and product variables difficult to represent mathematically. Other modules (E4.4 through E4.6) have shown how various models (mathematical representations) for nonideal reactors may be formulated and applied to reactor design and analysis. For example, a real reactor whose mixing characteristics fall between ideal plug flow and perfect mixing can be modeled as a series of perfect mixers. The same modules also demonstrate that tracer response measurements can provide the information needed to select a flow model for a reactor, and to determine the model parameters which best simulate the reactor behavior.

It is also possible, and often useful, to describe quantitatively the nature of flow and mixing in a reactor without resorting to specific models. This module introduces several concepts which form the basis of this approach.

As a simple illustration, let us first consider a chamber (system) with one inlet and one outlet, which contains thousands of white marbles (fluid molecules). Further suppose that hundreds of white marbles enter and leave the chamber each second.

Unless the marbles move uniformly through the system, the periods of time that they spend in the chamber before emerging vary about a mean value. Clearly (remembering that the chamber being discussed really represents a process system) how these times are distributed must have a significant effect on the performance of any process to be carried out in the chamber. One would therefore like to know...
how long each of the emerging marbles was in the chamber before emerging vary about a mean value.

Unfortunately, simply observing the emerging marbles cannot give us this information, since they all
look alike. The solution is to perform a tracer experiment. At an instant in time, which will be called
$t=0$, we introduce one hundred red marbles (tracer) into the inlet stream, and then position ourselves at
the outlet to observe the times at which red marbles emerge. Suppose that in a time interval from $t = 5$
seconds to $t = 6$ seconds we observe 15 red marbles.

We now know that of the red marbles entering the reactor, a fraction $15/100$ had residence times between
3 seconds and 6 seconds, since all of the red marbles entered together at $t = 0$. If we assume that the red
marbles behave exactly as the white ones do (i.e. that the tracer is perfect) and that the system is at steady-
state, we can estimate that of all the marbles entering the system, 15% remain there for a period between 3
and 6 seconds. It follows that 15% of all the marbles in the exit stream were in the system for the same
time interval. If we had injected 1000 marbles and observed 150 we would have greater confidence in
this conclusion; still more if we had injected roughly $10^{20}$ marbles and counted $0.15 \times 10^{20}$, which is
closer to what happens in a real tracer experiment.

We can perform the same calculation for arbitrary 1-second intervals, and plot the results versus time
from injection. The plot might appear as in Figure 1. This histogram provides an estimate of the residence
time density function for marbles in the outflow. (It can also be identified as an estimate of the system impulse
response function, defined in Module E4.4.)

It is this type of information that we wish to obtain about process vessels and reactors. In this module we
define a set of functions which describe residence time distributions of fluid elements in a process unit,
present the relationships that exist among them, and show how to determine them from tracer experiments.

RESIDENCE TIME DENSITY FUNCTION

Definition

Let us consider a system with one inlet and one outlet (Figure 2). The residence time density function (or
exit age density) of fluid elements in the system, designated $E(t)$, is formally defined as follows:

$$\int_0^1 E(t)\,dt$$

The fraction of emergent fluid elements that were in the system for a time between $t$ and $t+\,dt$ is equal to
the fraction of the outflow that was in the system for a time between $t_1$ and $t_2$ equals the sum of the
fractions with residence times in all differential intervals between these limits. or

$$\int_0^1 E(t)\,dt$$

The residence time distribution, $F(t)$ is:

$$\int_0^t E(t')\,dt' = \begin{cases} \text{fraction of outflow with residence times} \\
\text{less than } t \end{cases}$$

The residence time distribution must satisfy the following conditions:

a) $E(t)=0$ for $t<0$ since no fluid can exit before it entered
b) $E(t) \leq 0$ for $t \geq 0$ since mass fractions are always positive

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

Why must this be so?

The residence time density function for a process unit might appear as shown in Figure 3 (recall the histogram
of the previous section). This plot shows that almost all fluid elements remain in the system between one and four
minutes, and on the average, spend approximately two minutes there. Later, a more precise definition of mean
residence time will be given.

Note that since $E(t)$ is a fraction, and therefore dimensionless, $E$ itself must have units of inverse time.
(In probabilistic terms, $E$ is a density rather than a distribution; nevertheless, let us call it a distribution,
following traditional reaction engineering usage.) $E(t)$ is the fundamental indicator of the flow and mixing
pattern in a process unit, and consequently, its measurement is an important step in the analysis of
nonideal reactors.

![Figure 1](image1.png)

**Figure 1.**

![Figure 3](image3.png)

**Figure 3.**
Determination of $E(t)$ from a tracer impulse response

Suppose a tracer is injected at the inlet of a process unit, and the response at the outlet is monitored. The following conditions are assumed to hold:

1. Constant flow rate $q$ (cm$^3$/s) and fluid density $\rho$ (g/cm$^3$).
2. Only one flowing phase.
3. "Closed" system—input and output by bulk flow only (no diffusion takes place across system boundaries).
4. Flat velocity profiles at the inlet and outlet.
5. Linearity with respect to the tracer: that is, the magnitude of the response at the outlet is directly proportional to the amount of tracer injected.
6. The tracer is completely conserved within the system, and is identical to the process fluid in its flow and mixing behavior.

In a time period from $t=0$ to $t=\Delta t$ seconds, a quantity $m_i$ (g) of a tracer is introduced at the reactor inlet, and the tracer concentration $c(t)$ (g/cm$^3$) in the effluent from the reactor is measured. (Eventually, $\Delta t$ will be allowed to approach 0, so that the injection is a true impulse; for now, simply assume that $\Delta t$ has an infinitesimally small fixed value.) Subject to the six stated conditions, the residence time density function in the system may be determined from the measured tracer response as

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

\left[
\begin{array}{c}
\text{Tracer concentration in the outflow (or a quantity proportional to it) at time } t \\
\text{Total area under tracer concentration (or a quantity proportional to it) curve versus time as measured at the outflow}
\end{array}
\right]

(1)

Finally, dividing by $dt$, gives

$$E(t)=\frac{qc(t)}{m_i}

(2)

Equation 2 can be used to determine $E(t)$ from a measured response function $c(t)$ if both the volumetric flow rate, $q$, and the mass of tracer injected, $m_i$, are known. One may avoid these requirements, however, by noting that since $qc(t)dt$ is the mass of tracer emerging in the interval from $t$ to $(t+dt)$, the total quantity of the tracer must be given by the relation

$$m_i=\int_0^\infty qc(t)dt

\downarrow

\frac{m_i}{q} = \int_0^\infty qc(t)dt

(3)

This is an expression of a material balance on the tracer (see Module E4.4). If this expression is substituted into Equation 2, the result is

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

(1)

which completes the proof.

Equation 1 may be put in an even more useful form. As a rule, the concentration of tracer in the output stream is not measured directly; instead, a quantity $R_i(t)$ which is proportional to $c(t)$ is
measured ($R_i$ denotes impulse response)—perhaps a counting rate if a radiotracer is used, or a light absorbance if the tracer is a dye, or a conductance if an electrolyte is the tracer. If $x(t) = k R_i(t)$, where $k$ is the constant of proportionality, and this expression is substituted into Equation 1, the constant cancels, leaving as the result:

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

(4)

To repeat, $R_i(t)$ is the response of a system to an impulse injection of a tracer, and $E(t)$ is the residence time density function.

**Example 1: Residence Time Density From a Tracer Impulse Response**

An idealized response to an impulse injection of tracer is shown in Figure 4. Determine the residence time density function.

**Solution:**

Let us first find the normalizing factor, $\int_0^\infty R_i(t) dt$, which is equal to the area under the tracer response curve. This particular curve can be represented by:

$$R_i(t) = \begin{cases} 0.3 (t - 10) & 10 \leq t \leq 20 \\ 0.3 (30 - t) & 20 < t \leq 30 \\ 0 & \text{everywhere else} \end{cases}$$

The area under the curve is 30 (counts). From Equation 1,

$$E(t) = \frac{R_i(t)}{\int_0^\infty R_i(t) dt} = \begin{cases} 0.01 (t - 10) & 10 \leq t \leq 20 \\ 0.01 (30 - t) & 20 < t \leq 30 \\ 0 & \text{everywhere else} \end{cases}$$

See Figure 5. Verify that $E(t)$ has the three properties of a residence time density function listed previously.

Now, let us consider why the assumptions previously listed in the determination of $E(t)$ from a trace impulse response are necessary. Certainly Assumption 1 is required; if conditions were not steady state, then the determined function $E(t)$ would depend upon the time the tracer experiment was performed. If the process fluid density varied, one could not balance input and output in terms of volumetric flow rates.

Assumption 2 is required, because if more than one flowing phase existed, the age-density function for the tracer would depend on whether the tracer were introduced into one or both phases, and on how it distributed itself between the phases within the system. Assumption 3, of a "closed" system, is needed since in all mass balances the product $qc$ is used for input and output terms, whereas if the system were not closed, dispersion (diffusion) terms would need to be added. (See Module E4.6). If Assumption 4 (flat velocity profiles) was not valid, the response signal would depend on how the tracer is distributed over the inlet and outlet cross sections, and its interpretation would be ambiguous.

The linearity assumption (Assumption 5) guarantees that if one doubled the mass $m_i$ of the tracer injected, the response would double in amplitude, but its form would not change. If the system were nonlinear, $E(t)$ calculated from Equation 4 would depend on the amount of tracer injected. Finally, the assumption of a perfect tracer (Assumption 6) is needed since one is really measuring the residence time distribution of the tracer and from it, inferring the residence time distribution of the carrier fluid. If the tracer behaved differently from the carrier fluid, the two functions would not be the same.

**Determination of Mean Residence Time**

The average residence time, $\bar{t}_E$, of the fluid in the outflow (the apparent mean residence time) is by definition the mean (first moment) of the residence time density function:

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

(5)

For example, the average residence time of the fluid in the reactor of Example 1 is:

$$\bar{t}_E = \int_0^\infty t E(t) dt = \int_{10}^{20} 0.01 t (t - 10) dt + \int_{20}^{30} 0.01 t (30 - t) dt = 20 \text{ seconds}$$

If the expression for $E(t)$ of Equation 4 is substituted in Equation 5, the result is

$$\bar{t}_E = \frac{\int_0^\infty t R_i(t) dt}{\int_0^\infty R_i(t) dt}$$

(6)

Thus, the mean of the residence time distribution may be determined directly from a measured impulse response.

Provided that certain conditions are satisfied, the mean of the residence time density function $\bar{t}_E$ defined by Equation 5, equals the nominal mean residence time.
\[ \bar{t} = \text{volume/volumetric flow rate:} \]
\[ \bar{t}_e = \bar{t} \quad \text{or} \quad \int_0^t t E(t) dt = \frac{V}{q} \quad (7) \]

For all practical purposes, the criteria for the validity of Equation 7 are the six conditions given at the beginning of this section.

**RESIDENCE TIME DISTRIBUTION (CUMULATIVE AGE DISTRIBUTION)**

**Definition**

\[ F(t) = \text{fraction of the fluid elements emerging in the outflow which were in the system less than time t}. \]

The relationship between \( F(t) \) and the residence time density \( E(t) \) is readily established.

\[ F(t) = \int_0^t E(t') dt' \quad (8) \]

Thus, the residence time or cumulative age distribution \( F(t) \) can also be determined from a tracer impulse response using Equations 4 and 8. From its definition, one can readily deduce the following properties of \( F(t) \):

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

b) \( F(t) \geq 0 \quad \text{when} \quad t \geq 0 \)

c) \( F(\infty) = 1 \)

and

\[ \frac{dF}{dt} = E(t) > 0 \quad (9) \]

The cumulative exit age distribution is a nonnegative, monotone nondecreasing function, which has the general appearance of Figure 6.

**Example 2: Determination of \( F(t) \) from an impulse response**

An impulse response measurement was performed on a process system, and the idealized response shown in Figure 7 was obtained. Determine the cumulative age distribution for the system.

\[ R_1(t) = 5(2-t) \quad 1 \leq t \leq 2 \]
\[ = 0 \quad \text{elsewhere} \]
\[ \int_0^t R_1 dt = (0.5)(5)(1) = 2.5 \text{ s} \]

\[ E(t) = \frac{R_1}{\int_0^t R_1 dt} = 2(2-t) \quad 1 \leq t \leq 2 \]
\[ = 0 \quad \text{elsewhere} \]
\[ F(t) = \int_0^t 0dt = 0 \quad \text{for} \quad t \leq 1 \]
\[ = 0 + \int_1^t E(t')dt' = \left[ 4t' - (t')^2 \right]_1 \]
\[ = 4t - t^2 - 3 \quad \text{for} \quad 1 \leq t \leq 2 \]
\[ = F(2) + \int_2^t 0dt = 1 \quad \text{for} \quad t \geq 2 \]

This is shown in Figure 8.

**Determination of \( F(t) \) from a positive or negative tracer step response**

Let us again consider a tracer response experiment, only now suppose that instead of injecting a tracer impulse, one imposes a step input by switching at \( t = 0 \) from a feed of pure carrier fluid to a fluid containing a tracer at a concentration \( c_0 \)(g/cm³). If the tracer concentration \( c(t) \) was monitored at the output, the response might appear as shown in Figure 9 (Note that if the tracer is not lost in the reactor due to irreversible adsorption, reaction, or activity decay, the response curve asymptotes to the value of the inlet tracer concentration \( c_0 \)).

Our object is to determine the fraction of the outflow emerging at time \( t \) with a residence time less than \( \bar{t} \); that is, the fraction that entered the reactor after the switch to the tracer feed was
performed. Let us first consider a time interval from \( t \) to \( (t + dt) \).

a) Mass of tracer entering in \( dt \):

\[
m_a = q \left( \frac{\text{cm}^3}{\text{s}} \right) c_e \left( \frac{\text{g}}{\text{cm}^3} \right) dt \ (\text{s})
\]

b) Total mass of fluid entering in \( dt \):

\[
m_b = q \left( \frac{\text{cm}^3}{\text{s}} \right) \rho \left( \frac{\text{g}}{\text{cm}^3} \right) dt \ (\text{s})
\]

where \( \rho \) is the process fluid density.

Next, consider the outflow in a time interval from \( t \) to \( (t + dt) \).

c) Tracer in outflow:

\[
m_c = q \left( \frac{\text{cm}^3}{\text{s}} \right) \rho \left( \frac{\text{g}}{\text{cm}^3} \right) dt \ (\text{s})
\]

As noted, the tracer must have a residence time of \( t \) or less. It is also apparent that any carrier fluid that entered at the same time as the tracer must also have a residence time less than \( t \); moreover, if the tracer and carrier have the same residence time distribution (which, one assumes here they do), one may write

\[
\frac{\text{total fluid in outflow with}}{\text{residence time} < t} = \frac{\text{total fluid entering}}{\text{tracer entering}}
\]

from which, one obtains

d) Mass of fluid in outflow residence time less than \( t \):

\[
m_d = m_a \frac{m_b}{m_a} = q c_e \rho \frac{dt}{c_e}
\]

e) Total mass of fluid in outflow:

\[
m_c = q \left( \frac{\text{cm}^3}{\text{s}} \right) \rho \left( \frac{\text{g}}{\text{cm}^3} \right) dt \ (\text{s})
\]

f) \[
F(t) = \frac{\text{Mass of fluid in outflow with}}{\text{residence time} < t} \left( \frac{\text{Total mass of fluid in outflow}}{\text{tracer entering}} \right) = \frac{m_d}{m_c} \tag{10}
\]

Finally, suppose that instead of measuring the tracer concentration \( c \) directly, a signal \( R_s \) proportional to \( c \) was measured, so that \( c = k R_s \) (and \( c_e = k R_{so} \)). Substituting for \( c \) and \( c_e \) in Equation 10, the proportionality constant \( k \) cancels, leaving us with the result

\[
F(t) = \frac{R_s(t)}{R_{so}} \tag{11}
\]

Thus, one may determine the cumulative age distribution \( F(t) \) from a measured step response \( R_s(t) \), simply by normalizing the response by its asymptotic value \( R_{so} \).

Sometimes it is more convenient to switch off the flow of a tracer at a given instant; i.e., to impose a negative step input, as in Figure 10. It is not difficult to show that the \( R \) curve may be obtained from such a response as

\[
F(t) = 1 - \frac{R_{-s}(t)}{R_{-so}} \tag{12}
\]

Once \( F(t) \) is known, the residence time distribution \( E(t) \) may be calculated from Equation 9

\[
E(t) = \frac{dF}{dt} \tag{9}
\]

as the slope of the \( F \) curve. To perform this calculation requires graphical or numerical differentiation of a tracer response curve; this is usually a highly inaccurate procedure, and it is therefore preferable to determine \( E(t) \) directly from an impulse response at all possible.

The mean residence time can be determined from a step response, without first having to calculate \( E(t) \), using the relationship shown in Figure 11

\[
T_e = \int_0^\infty [1 - F(t)] dt \tag{13}
\]

Try to derive Equation 13 from Equations 5 and 9.

Note: In some references, \( F(t) \) is defined as the unit step response, or the response of a step input normalized by its asymptotic value, and another function is defined as the cumulative age distribution. The two are equivalent, as long as the six conditions stated at the beginning of the previous section are satisfied.

Example 3: Step Response Analysis

Determine \( F(t) \), \( T_e \), and \( E(t) \) from the step response in Figure 12.

Solution:

\[
R_{so} = 10 \Rightarrow F(t) = \frac{R_s}{R_{so}} = 0, \ t \leq 2
\]

\[
= t - 2, \ 2 \leq t \leq 3
\]

\[
= 1, \ t > 3
\]

![Figure 10.](image)

![Figure 11.](image)
function $E(t)$, then
\[ f(t)dt = f(\theta)d\theta \]
since the fraction with age between $t$ and $(t + dt)$ is numerically equal to the fraction with reduced age between $\theta$ and $(\theta + d\theta)$. Hence,
\[ f(\theta) = f(t) \frac{dt}{d\theta} = \bar{f}(t) \quad \text{(15)} \]
In particular:
\[ E(\theta) = \bar{t}E(t) \quad \text{(16)} \]
Observe that $E(\theta)$ is dimensionless [unlike $E(t)$, which has units of inverse time].

b) If $f(t)$ does not contain units of time, then:
\[ f(\theta) = F(t) \]
In particular:
\[ F(0) = F(t) \quad \text{(17)} \]
$E(0)$ and $F(t)$ are related simply as follows:
\[ E(\theta) = dF(\theta)/d\theta \quad \text{(18)} \]
\[ F(\theta) = \int_0^\theta E(\theta)d\theta \quad \text{(19)} \]

**Example 4: Evaluation of $E(\theta)$ and $F(\theta)$**

A radiotracer impulse is injected at the inlet of a reactor, and the response at the outlet is measured. The count rate $R$ (counts/s), after corrections for background and decay are applied as shown in Figure 14a, where the reactor volume is 20 liters, and the throughput rate is 2 L/min. Determine the density function $E(\theta)$.

**Solution:**

First determine $E(t)$ using Equation 4.
\[ E(t) \quad \text{(min}^{-1}) = \frac{R(t)}{\int_0^\infty R(t)dt} \]

Now, from Equation 16, $E(\theta) = \bar{t}E(t)$, and
\[ \bar{t} = 20(1)/(2(\text{L/min}) = 10 \text{ min} \]
Combining these results, obtains
\[ E(\theta) = \bar{t}E(t) = \frac{10R}{\int_0^\infty R(t)dt} \]
The area under the $R(t)$ curve may be calculated by graphical or numerical integration. Suppose the result is

$$\int_{t_0}^{t_f} R(t) dt = 25,000 \text{ cps} \cdot \text{min}$$

Then,

$$E(\theta) = \frac{10R}{25,000} = 4.0 \times 10^{-3} R$$

The value of $E(\theta)$ at the peak maximum and the corresponding reduced time are

$$E_{\text{max}} = 4.0 \times 10^{-3} R_{\text{max}} = 16$$

$$\theta_{\text{max}} = t_{\text{max}} / \bar{t} = 9 \text{ min} / 10 \text{ min} = 0.9$$

The curve might appear as shown in Figure 14b.

**DEVIAITION FROM IDEAL FLOW PATTERNS, STAGNANT ZONES, BYPASSING, INTERNAL RECIRCULATION**

Deviation from ideal flow patterns is most often determined by examining the shape of the $E(\theta)$ curve, since this function is readily obtainable from impulse tracer responses. $E(\theta)$ curves for systems with various degrees of axial mixing are shown in Figures 15a-15d. The shape of the $E$ curve may also suggest the existence of stagnant zones, bypassing and internal recycling, as illustrated in Figure 16. However, the $E$-curve does not necessarily reveal the occurrence of these phenomena; for example, a unimodal (one peak) $E$-curve may still be obtained in systems with bypassing and/or recycling.

In Module E4.5, it was shown that the stagnant volume fraction of a process unit may be obtained from an impulse response test in the following way. Suppose the impulse response appears as in Figure 17. Further suppose that the true reactor volume $V$ and the volumetric flow rate through the reactor $q$ (and therefore the true mean residence time $\bar{t} = V/q$) are known. Let $V'_e$ be the effective volume of the reactor—the total volume minus the stagnant volume—and say that $\bar{t}_e = V'_e/q$ is the apparent mean residence time. The percentage of the reactor which is stagnant is

$$PS = \frac{V - V'_e}{V} \times 100\% = \frac{\bar{t} - \bar{t}_e}{\bar{t}} \times 100\% \tag{20}$$

The question remains, how does one determine $\bar{t}_e$?

One may say that the portion of the response excluding the tail (i.e. up to the dashed line of the above plot) is essentially the impulse response of the active portion of the reactor. Hence, one eliminates (truncates) the tail, and substitutes the remainder of the response into Equation 6 to calculate $\bar{t}_e$. Once $\bar{t}_e$
is known, the percentage stagnancy may be determined from Equation 20.

Example 5: Detection of Stagnancy

A tracer is injected at the inlet of an 1100 liter process unit, through which 340 L/min are flowing. The mean residence time calculated from the truncated tracer response is $t = 2.5$ min. Estimate the percentage of the reactor volume which is stagnant.

Solution:

$$
t = \frac{V}{q} = \frac{(1100 \text{ L})}{(340 \text{ L/min})} = 3.24 \text{ min}
$$

$$
PS = \frac{3.24 - 2.5}{3.24} \times 100\% = 22.8\%
$$

Therefore, only about 77% of the reactor volume is being utilized effectively. Modification of the process unit design to improve mixing should be considered.

Considerable approximation is necessarily involved in stagnancy calculations: it is impossible to know exactly where to truncate the response, and more fundamentally, the "volume of the stagnant zone" is a fictional quantity to begin with. However, the engineer is only interested in knowing whether 60% or 80% of 100% of his reactor is being used effectively (whether it is 60% or 61% is of no practical concern), so that the approximations do not represent a real drawback to the method.

Example 6: Age Distribution Functions From Discrete Tracer Data in a Partially Stagnant System

The results of an impulse response experiment are presented in Table 1. The concentration of the tracer was monitored at one minute intervals at the outlet following an injection of 3800g of tracer. The flow rate through the reactor was maintained at 100(L/min) and the reactor volume is 800 liters. Find $E(t)$ and $F(t)$ for this vessel.

Solution:

From Figure 18, one can see that the tracer impulse response has a prolonged tail and therefore some stagnancy exists in the system. Note that with discrete data, one cannot be certain about the exact location of the peak.

First, let us determine whether the tracer material balance is satisfied (Equation 3):

$$
\frac{m_i}{q} = \int_0^\infty c(t)dt
$$

Given, is that $\frac{m_i}{q} = 38(\text{g} \cdot \text{min})/\text{L}$. The integral on the right may be calculated by Simpson's rule:

$$
\int_0^\infty c(t)dt \approx \frac{\Delta t}{3} \left[ c_0 + 4c_1 + 2c_2 + 4c_3 + \ldots + 2c_{n-1} + c_n \right]
$$

$$
= 36.47 \frac{\text{g} \cdot \text{min}}{\text{L}}
$$

The basic material balance is thus satisfied within 4%, and the determined area under the curve could be used directly for normalization and evaluation of the $E(t)$ curve. However, the contribution of the unmeasured tail of the tracer response curve to the total mass balance is often much larger, and the tail has to be approximated in some manner. Although this is not necessary in our example, let us use this opportunity to illustrate the procedure.

A commonly used method is to fit the data in the tail with an exponential function, $A \exp(-kt)$. The data past the peak are plotted versus time on a semilog plot, as shown in Figure 19. The linearity of the plot confirms the exponential functionality of the tail; the function parameters are $k = 0.23$ (min$^{-1}$) and $A = 12.55$ (g/L).

Now calculate the area under the curve using.

---

Table 1.

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<th>$c$ (g/L)</th>
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American Institute of Chemical Engineers
Simpson’s rule:
\[ \int_{0}^{\infty} c(t)dt = \frac{\Delta t}{3} \left[ c_1 + 4c_2 + 2c_3 + \ldots + 4c_{i0} + c_{i1} \right] \]
\[ + \int_{11}^{\infty} Ae^{-kt}dt = 32.60 + 4.34 = 36.94 \text{ min} \]
Now, by dividing each value of \( c \) in Table 1 by 36.94, obtain age density \( E(t) \). The apparent mean residence time \( \bar{t}_E \) can then be found as:
\[ \bar{t}_E = \int_{0}^{\infty} tE(t)dt = \frac{\Delta t}{3} \left[ t_1E(t_1) + 4t_2E(t_2) + 2t_3E(t_3) + \ldots + t_{i1}E(t_{i1}) \right] \]
\[ + \int_{11}^{\infty} Ate^{-kt}dt = 7.5 \text{ min} \]
The nominal mean residence time is \( \bar{V}/q = 8 \text{ min} \), which implies that about 6% of the volume of the vessel may be considered stagnant.

EXTENSION TO MULTIPHASE SYSTEMS

Many of the reactors encountered in practice involve heterogeneous systems with two or more phases, such as fluidized and moving bed reactors, gas-liquid packed or bubble column contactors, etc. The extension of the methods described in this module to such systems is straightforward.

Let us consider the two-phase system, shown in Figure 20. Phase II is stagnant while Phase I flows through the system with flow rate \( q \). Suppose at \( t = 0 \) one injects a quantity of tracer 1, which remains confined to Phase 1, and that \( R_1(t) \) is the measured response. From Equation 6,
\[ \int_{0}^{\infty} \frac{V_1}{q} \int_{0}^{\infty} \frac{tR_1(t)dt}{R_1(t)dt} \]
Now an impulse of another tracer which distributes itself between both phases is injected, with a partition coefficient \( K \):
\[ K = \frac{c_{2e}}{c_{1e}} \]
where \( c_{2e} \) is the equilibrium concentration of tracer 2 in Phase I and \( c_{1e} \) is that in Phase II. Then, if it can be assumed that the equilibrium distribution between the two phases is established very rapidly, the following expression can be written for the mean residence time of tracer 2:
\[ \frac{V_1 + KV_2}{q} \int_{0}^{\infty} \frac{tR_2(t)dt}{R_2(t)dt} \]
This provides a useful way of determining effective volumes in multiphase reactors. Note that the right-hand sides of Equations 21 and 23 are the means of density functions: \( E_i(t) \) is clearly the differential RTD for the flowing phase—how would one interpret \( E_2(t) \)?

NOMENCLATURE

\( c \) = tracer concentration in the outflow
\( c_0 \) = inlet tracer concentration for step inputs
\( E \) = exit age (residence time) density function
\( F \) = residence time distribution (cumulative age distribution)
\( f \) = probability density function
\( K \) = partition coefficient
\( m \) = fluid mass
\( m_t \) = mass of tracer injected in an impulse injection
\( \rho_s \) = density of tracer injected in an impulse injection
\( q \) = volumetric flow rate
\( R_1 \) = percentage of stagnant reactor volume
\( R_1 \) = step response
\( R_{-1} \) = step-down response
\( t \) = time
\( t_E \) = first moment of the exit age density function
\( \bar{t} \) = mean residence time
\( V \) = reactor volume
\( V_{eq} \) = effective (active) reactor volume

GREEK LETTERS

\( \theta \) = dimensionless time
\( \rho \) = fluid density

SUGGESTED COMPLEMENTARY READING

STUDY PROBLEMS

1. What is the physical significance of the function $E(t)$ for a flow reactor? (You may express your answer in terms of $E(t)dt$.) What about $F(t)$?

2. Explain how to determine $E(t)$ for a system from a measured tracer impulse response $R_s(t)$. How would you estimate the effective mean residence time from $E(t)$?

3. Explain how to determine $F(t)$ for a system from a measured tracer step response. How could one determine $E(t)$ from $F(t)$?

4. A hypothetical age density function is shown in Figure 21.
   a) Does the function satisfy the three conditions required of an $E$ function?
   b) What fraction of the emerging fluid was in the reactor less than 1 minute? Between 1 minute and 2 minutes? Between 1 minute and 3 minutes?

5. A hypothetical cumulative age distribution is shown in Figure 22.
   a) What fraction of the emerging fluid was in the reactor for 15 minutes or less.
   b) Sketch the $E$ curve for this reactor.

6. Under what conditions would you expect the mean of the residence time density,

$$\bar{E}_r = \int_0^\infty tE(t)dt$$

calculated from a measured impulse response, to differ from the nominal mean residence time $V'/q$?

7. The residence time densities in Figure 23 were obtained from impulse response measurements on different systems. The systems for which they were obtained are described below. Match the responses to the systems.
   a) A tubular reactor, close to ideal plug flow.
   b) A well-mixed continuous stirred tank reactor.
   c) A tubular reactor containing an orifice, on either side of which the fluid is relatively stagnant.
   d) A poorly packed reactor in which a channel has formed, through which a portion of the fluid passes much more rapidly than the bulk of the fluid.
   e) A catalytic reactor in which a fraction of the outlet stream is recycled back to join the feed stream.

HOMEWORK PROBLEMS

1. The following frames show measured impulse responses. For each one, determine and sketch the required distributions and calculate the requested quantities, assuming that $\bar{E}_r = \bar{F}$.

   a) $\bar{r}_1$

<table>
<thead>
<tr>
<th>Given</th>
<th>Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse Input</td>
<td>$V$, $\bar{F}$, $E(t)$</td>
</tr>
<tr>
<td>$q = 5 \text{ L/min}$</td>
<td>$F(t)$</td>
</tr>
</tbody>
</table>

   b) $\bar{c}$

<table>
<thead>
<tr>
<th>Given</th>
<th>Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse Input</td>
<td>$q$, $V$, $E(t)$, $E(t)$</td>
</tr>
<tr>
<td>$m_i = 0.050$, $q$</td>
<td>$E(t)$, $q$</td>
</tr>
</tbody>
</table>

   c) $\bar{E}_r$

<table>
<thead>
<tr>
<th>Given</th>
<th>Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impulse input</td>
<td>$V' = 500 \text{ L}$</td>
</tr>
</tbody>
</table>

   d) $\bar{F}$

<table>
<thead>
<tr>
<th>Given</th>
<th>Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impulse input</td>
<td>$\bar{F}$, $E(t)$, $F(t)$</td>
</tr>
</tbody>
</table>

2. The following frames show measured step responses. For each one, determine and sketch the required distributions and calculate the requested quantities, assuming that $\bar{E}_r = \bar{F}$.
3. Two grams of tracer are injected instantaneously into a flow reactor and the exit tracer concentration is monitored and shown in Figure 24. The flow rate is known to be 1.0 (L/min).

a) Is the tracer material balance equation satisfied?
b) Calculate the active volume of the system if the total volume is 3 liters, and the percentage of the volume that is stagnant.

4. A packed column 15 m high with a 1.0 m$^2$ cross section ($e = 0.5$) is used for gas-liquid contacting. Gas flows at 0.5 m$^3$/s through the unit and liquid flows at 0.05 m$^3$/s. We would like to know the volume fraction occupied by flowing gas, free flowing liquid and stagnant liquid trapped in the packing. A pulse of nonvolatile tracer is introduced into the entering liquid, and a step input of noncondensable tracer is injected at the gas inlet. The tracer concentrations are measured at the liquid and gas outlets. Using the data given in Figures 25 and 26, find the desired volume fractions, and sketch the gas and liquid residence time distributions.

5. Table 2 shows the impulse response obtained in a 10 liter liquid-phase reactor. Determine $t = t_1$ by numerical integration, and then generate plots of $E(t)$ and $F(t)$ versus $t$. Use the trapezoidal rule for integration.

Table 2.

<table>
<thead>
<tr>
<th>$t$ (min)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$ (g/L)</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
<td>1.2</td>
<td>7.0</td>
<td>12.0</td>
<td>9.0</td>
<td>7.0</td>
<td>5.8</td>
<td>5.0</td>
</tr>
<tr>
<td>$t$ (min)</td>
<td>15</td>
<td>20</td>
<td>25</td>
<td>30</td>
<td>45</td>
<td>60</td>
<td>75</td>
<td>90</td>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c$ (g/L)</td>
<td>3.5</td>
<td>2.8</td>
<td>2.3</td>
<td>1.9</td>
<td>1.0</td>
<td>0.5</td>
<td>0.3</td>
<td>(0.1)</td>
<td>(0)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1. \( E(t) \) is the fraction of the emerging fluid which was in the reactor for a time between \( t \) and \( (t + dt) \). \( F(t) \) is the fraction which was in the reactor for a time less than \( t \).

2. Integrate the response graphically or numerically to determine the area under the curve

\[
\int_{0}^{\infty} R_I(t) \, dt
\]

Then calculate the \( E \) function as

\[
E(t) = \frac{R_I(t)}{\int_{0}^{\infty} R_I(t) \, dt}
\]

and determine \( \bar{E} \) from Eq. (5).

3. Use Eq. (16) to determine \( F(t) \) from a positive step response, or Eq. (17) to determine \( F \) from a negative step response. \( E(t) \) can be calculated as the slope of the \( F(t) \) curve.

4. (a) \( E(t) = 0 \) for \( t < 0 \), \( E(t) > 0 \) for \( t > 0 \), and

\[
\int_{0}^{\infty} E(t) \, dt = 0.25(2-1) + 0.75(3-2) = 1, \text{ therefore, yes.}
\]

(b) \( \boxed{\text{None.}} \)

\[
\int_{1}^{2} E(t) \, dt = 0.25 \quad \int_{1}^{3} E(t) \, dt = 1.0
\]

5. (a) \( F(t) = \frac{t}{25}, \ t \leq 25 \)

\[
= 1.0 \quad t > 25
\]

Fraction \( < 15 = F(15) = \frac{15}{25} = \boxed{0.6} \)
6. If a significant portion of the reactor volume is stagnant, then $\bar{t} \neq t_E$.

7. 1b, 2c, 3a, 4e, 5d
Mixing Effects in Chemical Reactors—V
—Micromixing and the Segregated Flow Model

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OBJECTIVES
At the completion of this module, the student should be able to:
1. Define the concepts of earliness and lateness of mixing, macrofluid and microfluid, segregation, macromixing, and micromixing; and recognize the roles of these concepts in the behavior of chemical reactors.
2. Define the segregated flow model, and calculate conversions based on the model for any residence time distribution and kinetic scheme.
3. State whether the conversion calculated assuming segregated flow represents an upper bound, a lower bound, or an exact estimate of the conversion that can be achieved in a reactor with a given residence time distribution.

PREREQUISITE MATHEMATICAL SKILL
1. Differential and integral Calculus.

PREREQUISITE ENGINEERING AND SCIENCE SKILLS
1. Kinetic rate laws and design equations for ideal plug flow and stirred tank reactors.
Residence time distributions (Module E4.7); mixing in chemical reactors (Modules E4.4, E4.5).

We have seen that the behavior of real chemical reactors may resemble neither ideal plug flow nor perfect mixing. Tracer tests can tell us whether a reactor flow pattern may be approximated as one or another of these ideal types (Module E4.4); if it cannot, the parameters of an appropriate model for nonideal flow, such as the dispersion model or tanks-in-series model (Modules E4.5 and E4.6) may be determined from the tracer response, and the model may then be used to predict reactor performance.

There is nothing unique about a model determined in this manner, however. While every real system has a unique residence time distribution (Module E4.7), a given residence time distribution may correspond to many different systems, and hence may be reproduced by many alternative models.

Several questions arise in this regard.
1. Can two reactive systems have the same residence time distribution, and yet yield different reactant conversions or product selectivities?
2. If the answer to the first question is yes (it is), what besides the RTD affects the reactor performance for a given reaction and rate law?
3. If the residence time distribution for a reactor is...
known, can the reactor performance be predicted directly without having recourse to a model such as those mentioned in the first paragraph? If so, how?

4. For a given residence time distribution, how much variation exists between the possible values of reactant conversion?

We will propose answers to each of these questions in this module.

**EARLIENESS OF MIXING**

Let us consider an ideal plug flow reactor and a perfect mixer with equal volumes in series. See Figure 1. A second-order reaction \( A \to R \), \( k = 10 \text{ L/mol \cdot min} \), is carried out in this system. The question is, does the order of the reactors make any difference in the conversion obtained?

Let us suppose that someone performed a tracer impulse response measurement on each of the two possible reactor arrangements. The results, yielding the residence time density function, which are shown in Figure 2, would be identical.

\[
E(t) = 0, \quad t < \bar{\tau}/2
\]

\[
= \frac{2}{\bar{\tau}} \exp \left[ -2(t - \bar{\tau}/2)/\bar{\tau} \right], \quad t \geq \bar{\tau} \tag{1}
\]

where \( \bar{\tau} \) is the total mean residence time in the two reactors. If the system performance were determined entirely by the residence time distribution, the order of the two reactors would obviously make no difference; yet, the order does make a difference. Let \( \bar{\tau}/2 = 0.5 \text{ min} \), and \( C_{A0} = 1.0 \text{ mol/L} \).

**PFR-CSTR:**

The design equation for the plug flow section is:

\[
\tau = \bar{\tau}_{\text{PFR}} = \frac{\bar{\tau}}{2}
\]

\[
= \int \frac{C_{A0}}{kC_A^2} \frac{dC_A}{C_{A1} - C_{A0}} = \frac{1}{k} \left[ \frac{1}{C_{A1} - C_{A0}} \right]
\]

\[
(2)
\]

and that for the perfect mixer is:

\[
\tau = \bar{\tau}_{\text{CSTR}} = \frac{C_{A1} - C_{A2}}{kC_A^2}
\]

\[
\tag{3}
\]

From these two equations, the intermediate concentration \( C_{A1} \) and the final reactant concentration \( C_{A2} \) can be readily calculated:

\[
C_{A1} = \frac{2C_{A0}}{2 + k\bar{\tau}C_{A0}} = \frac{1}{2 + 10} = 0.1667 \text{ (mol/L)}
\]

\[
(4)
\]

\[
C_{A2} = \frac{-1 + \sqrt{1 + 2k\bar{\tau}C_{A1}}}{k\bar{\tau}} = \frac{-1 + \sqrt{1 + 20 \times 0.1667}}{10}
\]

\[
= 0.1082 \text{ (mol/L)}
\]

(Verify these equations.) The final conversion is:

\[
x_4 = 1 - \frac{C_{A2}}{C_{A0}} = 0.892
\]

**CSTR-PFR:**

The design equations are

\[
\tau = \frac{\bar{\tau}}{2} = \frac{C_{A0} - C_{A1}'}{kC_{A1}'}^2
\]

\[
(7)
\]

\[
\tau = \bar{\tau} = \int \frac{C_{A1}'}{kC_{A1}^2} \frac{dC_{A1}'}{C_{A2} - C_{A1}'}
\]

\[
(8)
\]

The intermediate and final concentrations are:

\[
C_{A1}' = \frac{-1 + \sqrt{1 + 2k\bar{\tau}C_{A0}}}{k\bar{\tau}} = \frac{-1 + \sqrt{1 + 20}}{10} = 0.3582 \text{ (mol/L)}
\]

\[
(9)
\]

\[
C_{A2} = \frac{1 + k\bar{\tau}/2}{\bar{\tau}C_{A1}} = \frac{0.3582}{1 + 5 \times 0.3582} = 0.1283 \text{ (mol/L)}
\]

\[
(10)
\]

The final conversion is

\[
x_4 = 1 - \frac{C_{A2}}{C_{A0}} = 0.872 \neq 0.892
\]

Let us consider the differences between the configurations that might have led to the different conversions. A second-order reaction is favored by a high reactant concentration; for example, doubling \( C_A \) quadruples the rate. In a plug flow reactor the concentration decreases gradually from its maximum value, whereas in a CSTR the decrease is abrupt. Placing the PFR first in the sequence keeps the
concentration as high as possible for as long as possible, and so yields a higher conversion than the reverse placement.

Viewed another way, in an ideal PFR all fluid elements age at the same rate. In the PFR-CSTR arrangement, mixing between fluid elements of different ages is therefore delayed as long as possible, while in the CSTR-PFR arrangement, elements entering the system are immediately mixed with other elements of different ages. The result just obtained suggests, at least for a second-order reaction, that the reactor performance is affected both by the age distribution at the outlet and by the earliness or lateness of the mixing required to achieve this distribution.

Later, this result will be generalized to show that for a given residence time distribution, early mixing increases conversion for reaction orders less than one, has no effect on first-order reactions, and decreases conversion for reaction orders greater than one. It may also be shown that earliness of mixing has an even greater effect on product distributions in multiple reaction systems than on reactant conversion in a single reaction.

**STATES OF AGGREGATION AND MICROMIXING**

This and previous modules have referred rather casually to “fluid elements,” without ever really saying what was meant. Let us now define a fluid element, or “clump,” as a group of molecules small enough to occupy no more than a microscopic volume (a “point”) in the reactor, but large enough for the concept of reactant concentration to be meaningful. As a rough estimate, a clump may be considered to contain 10^{10} molecules, give or take five orders of magnitude.

Two extreme states of aggregation of a process fluid are represented schematically in Figure 3, and are referred to as macrofluid and microfluid. In a macrofluid, molecules move together in clumps; the clumps are distributed in residence times, but all molecules within a clump have the same age. In a microfluid, the clumps are dispersed; all molecules move independently of one another, regardless of age.

A real process fluid is generally neither a macrofluid nor a microfluid, but may approach one or the other of these extremes. For example, in a spray tower the liquid may be considered a macrofluid and the gas a microfluid, and vice versa in a bubble tower. Viscous elastomers are much more likely to behave as macrofluids than gases and low viscosity liquids.

In general, however, the state of aggregation of a fluid depends on various physical properties, the apparatus in which the operation takes place, the flow fields to which the fluid is subjected, and the residence time in the process unit. The aggregative state may be guessed at using intuition and perhaps turbulence and mixing theory, but it cannot be predicted with certainty.

The residence time distribution in a reactor is in a sense a measure of the degree to which fluid elements (clumps) mix: in an ideal plug flow reactor no mixing occurs, while in a perfect mixer there is uniformity among elements of different ages. It has also been seen, however, that mixing on another level occurs, namely, between molecules in different fluid elements. The terms macromixing and micromixing are used to denote these two mixing modes. Another term is the segregation of a system, meaning the extent to which micromixing is negligible. Saying that a fluid is completely segregated is the same as saying that it is a macrofluid.

Two conceptual models have been developed to describe the extreme cases of segregation.

**Segregated flow model**

The process fluid behaves as a macrofluid. Some clumps exit early, others late, as required by the residence time distribution, but the molecules in each clump are surrounded only by molecules of the same age at all times. Mixing of molecules of different ages occurs as late as possible, that is, at the reactor exit where the outflow is formed.

**Maximum mixedness model**

The molecules of the feed immediately upon entering mix and become associated with the molecules in whose company they will eventually leave the reactor.

Mixing that falls short of complete segregation is referred to as partially segregated flow. Figures 4a and 4b illustrate segregated and partially segregated flow. The system is viewed as being able to accommodate 6 fluid clumps of four subelements apiece. At fixed time increments, 3 clumps leave the system and 3 new clumps enter in their place. Between increments the subelements may mix to form new clumps with distributed ages.

Figures 4a and 4b show the ages of all fluid subelements in the system and in the exiting fluid when the system is at steady state. The age of a subelement in the reactor is the time that has elapsed.
since the subelement entered the reactor, and the exit age (residence time) in the effluent fluid is the time the subelement spent in the reactor. An age of one for a subelement in the system indicates an age less than one time period in the system, while age 2 indicates an age greater than or equal to one but less than two periods, and age 3 indicates an age larger than or equal to two but less than three periods. In the effluent fluid age one indicates a residence time equal to or greater than one period but less than two, and exit age 2 and 3 are defined in the same manner. Note that the residence time distribution is the same for both models in Figure 4: a third of the emerging molecules have ages of one, a third have ages of 2, and one third have ages of 3.

In segregated flow the fluid behaves as if the boundaries of each clump were impermeable. The fluid is completely segregated by age, and no mixing between elements of various ages occurs until the exit is reached. If reaction were taking place, each of the clumps would behave like a batch reactor, with the reaction time being equal to the residence time of the clump.

In Figure 4b, the dashed lines may be viewed as permeable boundaries. In every time period the boundaries break, and the contents are mixed with the incoming fluid to form new loose clusters.

Procedures have been derived to predict the performance of a reactor in the extremes of segregated flow and maximum mixedness, and it has also been shown that these two models provide the bounds for conversion that can be achieved for a single nth-order reaction and a specified residence time distribution. The maximum mixedness formula is difficult to implement, generally requiring the numerical solution of a differential equation (3), and will not be discussed further. The next section illustrates the application of the segregated flow model to reactor analysis.

SEGREGATED FLOW MODEL

Consider a segregated flow reactor with a known residence time distribution, in which a reaction \( A \rightarrow R \) with a rate of disappearance of \( A \) given by \([-r_A(C_A)]\). \( r_A(C_A) \) takes place. See Figure 5. Since the fluid flows in clumps and is completely segregated by age, each clump behaves like a batch reactor. For a constant density fluid, one can calculate the reactant concentration in every clump from:

\[
-\left( \frac{dC_A}{dt} \right)_{clump} = r_A(C_A_{\text{clump}}) \tag{12}
\]

which may be integrated to yield:

\[
\int_{C_{\text{AO}}}^{C_{\text{Aclump}}} \frac{dC_A}{r_A(C_A)} = t \tag{13}
\]

From Equation 13, \( C_{\text{Aclump}} \) can be determined explicitly as a function of time for all nth-order reactions, and for other rate laws an implicit relationship may be obtained. The mean concentration in the outflow can be found as follows:

\[
\left( \begin{array}{c}
\text{mean concentration} \\
\text{of reactant in} \\
\text{exit stream}
\end{array} \right) = \bar{C}_A = \lim_{\Delta t \to 0} \frac{1}{n} \sum_{\text{all elements of exit stream}} \left( \begin{array}{c}
\text{concentration} \\
\text{of reactant remaining in} \\
\text{an element (clump) of age} \\
\text{between } t \text{ and } (t + \Delta t)
\end{array} \right)
\]

\[
= \bar{C}_A = \lim_{\Delta t \to 0} \int_{t}^{t + \Delta t} \left( \begin{array}{c}
\text{fraction of} \\
\text{exit stream} \\
\text{which is of} \\
\text{age between} \\
\text{t and } (t + \Delta t)
\end{array} \right)
\]

Using Equation 12 for the reactant concentration remaining in an element that has been in the reactor for a time \( t \), and recalling that by definition, \( E(t)dt = \) the fraction of the exit stream with ages between \( t \) and \( (t + dt) \), one obtains

\[
\bar{C}_A = \int_{0}^{\infty} C_{A\text{clump}}(t)E(t)dt \tag{14}
\]

The reactant conversion is \( x_A = \frac{1 - \bar{C}_A}{C_{\text{AO}}} \), so that

\[
1 - x_A = \int_{0}^{\infty} \left( \frac{\bar{C}_A}{C_{\text{AO}}} \right)_{\text{clump}} E(t)dt \tag{15}
\]

Example 1:

A first-order reaction \((k = 2 \text{ min}^{-1})\) is carried out in a flow reactor with the following residence time distribution:

\[ E(t) = 0 \text{ when } t < 1 \text{ min} \]

\[ = \exp(1 - t) \text{ when } t \geq 1 \text{ min} \]

Estimate the fractional conversion using the segregated flow model.
**Solution:**

For a first-order reaction,

\[
\frac{C_A}{C_{AO,\text{d}ump}} = \exp(-kt) = \exp(-2t)
\]

From Equation 15,

\[
1 - x_t = \int_0^\infty \frac{C_A}{C_{AO,\text{d}ump}} E(t) dt = \int_1^\infty \exp(1 - 3t) dt = -\frac{1}{3} \exp(1 - 3t)\bigg|_1^\infty = 0.0451
\]

Therefore,

\[
x_t = 0.955
\]

**Example 2:**

An impulse tracer test produced the exit age density function presented in Table 1, for a reactor in which a first-order reaction with rate constant \(k = 0.1 \text{ min}^{-1}\) is taking place. Find the reactant conversion at the same operating conditions at which the tracer test was performed.

**Solution:**

Let us first verify that \(E(t)\) is properly normalized, using Simpson's rule to perform the integration.

\[
\int_0^\infty E(t) dt = \frac{\Delta t}{3} \left[ E_1 + 4(E_2 + E_4 + \ldots E_{2n}) + 2(E_3 + \ldots E_{2n-1} + \ldots + E_{2n}) \right] = \frac{5}{3} \{0.0 + 4[0.03 + 0.05 + 0.02 + 0.002] + 2[0.050 + 0.040 + 0.010] + 0.0\} = 1.0
\]

The table can now be extended; see Table 2.

Then from Equation 15,

\[
1 - x_t = \int_0^\infty e^{-kt} E(t) dt \to 0.288
\]

or

\[
x_t = 0.712
\]

The mean residence time in the reactor is

\[
\bar{t} = \int_0^\infty t E(t) dt \to 15.13 \text{ min}
\]

If ideal plug flow is assumed for the reactor,

\[
1 - x_t = e^{-\bar{t} \cdot \bar{C}_t} = e^{-5.13} = 0.220 \Rightarrow x_{40FR} = 0.780
\]

and if perfect mixing is assumed

\[
1 - x_t = \frac{1}{1 + kt} = \frac{1}{1 + 1.513} = 0.398 \Rightarrow x_{ACSTR} = 0.602
\]

As expected the conversion based on the actual residence time distribution lies between these two extremes.

**Example 3:**

Evaluate the conversion for a second-order reaction with rate constant \(k = 10 \text{ L/mol} \cdot \text{min}\) in a reactor with the residence time distribution of a perfect mixer, assuming segregated flow. The feed reactant concentration is \(C_{AO} = 1 \text{ (mol/L)}\) and the mean residence time is \(\bar{t} = 1 \text{ min}\). Then compare the calculated conversion with that which would be achieved if the reactor contents behaved as a microfluid.

**Solution:**

The residence time density function

\[
E(t) = \frac{1}{\bar{t}} e^{-\bar{t} t} = e^{-t}
\]

The clump concentration is

\[
\frac{C_A}{C_{AO,\text{d}ump}} = \frac{1}{1 + ktC_{AO}} = \frac{1}{1 + 10 t}
\]

<table>
<thead>
<tr>
<th>Table 1.</th>
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<tbody>
<tr>
<td>(t) (\text{min})</td>
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<td>(E(t)) (\text{min}^{-1})</td>
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<td>(t) (\text{min})</td>
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<td>(E(t)) (\text{min}^{-1})</td>
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<tr>
<td>(e^{-kt} E(t))</td>
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<tr>
<td>(t E(t))</td>
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</table>
The segregated flow model, Equation 15, predicts

$$1 - x_A = \int_0^\infty \frac{1}{1 + kiC_{ao}} \frac{1}{1 + 10t} e^{-10t} dt = \int_0^\infty \frac{e^{-10t}}{1 + 10t} dt = 0.1e^{-1.1x}$$

This integral may be evaluated in terms of a tabulated function called the exponential integral (see Homework Problem 3) or it may be integrated numerically. The result is

$$1 - x_A = 0.201 \Rightarrow x_A = 0.799$$

Recall that when the earliness and lateness of mixing was discussed at the beginning of this module, it was shown that late mixing favors higher conversions for second-order reactions. One would suspect, since segregated flow implies the latest possible mixing, that conversion in a segregated perfect mixer is higher than in the one in which a microfluid is ideally mixed. The familiar design equation for an ideal CSTR,

$$\bar{t} = \frac{C_{ao} - C_A}{-r_A(C_A)}$$

presumes that the fluid in the tank is completely homogeneous in composition, that is, a microfluid. Substituting a second-order rate law for $-r_A$ in this equation eventually yields:

$$1 - x_A = \frac{(1 + 4kiC_{ao})^{1/2} - 1}{2kiC_{ao}}$$

If,

- $k = 10$ (L/mol·min)
- $\bar{t} = 1$ (min)
- $C_{ao} = 1$ (mol/L)

then,

$$1 - x_A = 0.270$$

and,

$$x_A = 0.730 < (x_A)_{\text{segregated flow}}$$

Thus, as expected, the conversion in segregated flow is higher than that obtained if the reactor contains a microfluid.

**EFFECT OF MICROMIXING ON CONVERSION**

The final result of the last example may be generalized by determining how micromixing affects reactor performance for a reaction of arbitrary order. Let us consider a single reaction

$$A \rightarrow R, \quad -r_A = kC_A^n$$

taking place in a flow reactor with an arbitrary residence time distribution. Let us make the following claims:

1. *For a first-order reaction (or a series of first-order reactions), micromixing has no effect on the reactor performance.* Conversion is thus predicted exactly by the segregated flow model (Equation 15).
\[ -r_A \text{ versus } C_A, \text{ coming up to this line from the} \]
\[ \text{midpoint of } C_{A1} \text{ and } C_{A2} \text{ on the abscissa, and reading} \]
\[ \text{the rate at the intersection (see Figure 6).} \]

Now suppose the elements are mixed completely.

The uniform reactant concentration in the combined element is

\[ C_{A_n} = \frac{1}{2} \left( C_{A1} + C_{A2} \right) \]

The rate of reaction \(-r_A\) is the value of \(-r\),

\[ \text{corresponding to this concentration; it is found} \]
\[ \text{graphically by proceeding vertically from } C_{A_n} \text{ to the} \]
\[ \text{rate curve, and reading the value of } -r_A \text{ at the} \]
\[ \text{intersection.} \]

It is clear from Figure 6a that if \(n < 1\), \(-\tilde{r}_A < -r_A\):

that is, mixing of fluid elements of different ages increases the average reaction rate, and hence the conversion. For \(n = 1\) (Figure 6b) mixing of elements of different ages has no effect on the average rate, and for \(n < 1\) (Figure 6c), micromixing decreases conversion \((-\tilde{r}_A < -r_A\). Similar arguments apply for two elements of unequal volumes, and for an arbitrary number of elements.

Example 4:

A zero-order reaction \(A \rightarrow R, -r_A = 9 \text{ mol/min}\), is

\[ \text{carried out in a perfect mixer. The mean residence time is } t = 1 \text{ min, and the feed enters at } C_{A0} = 10 \]
\[ \text{mol/L}. \text{ Calculate the fractional conversion that will} \]
\[ \text{be achieved a) in segregated flow, b) if the reactor} \]
\[ \text{contains a microfluid.} \]

Solution

a) Segregated flow

\[ -r_A = \frac{dC_A}{dt} = 9 \left( \frac{C_A}{C_{A0}} \right)_{\text{clump}} \]

\[ = 1.0 - 0.9t \text{ when } t \leq \frac{10}{9} \]

\[ = 0 \text{ when } t > \frac{10}{9} \]

\[ E(t) = \frac{1}{t} e^{-t} = e^{-t} \]

\[ 1 - x_A = \int_0^t \left( \frac{C_A}{C_{A0}} \right)_{\text{clump}} E(t) dt \]

\[ = \int_0^{10/9} (1.0 - 0.9t)e^{-t} dt = 0.396 \]

and therefore,

\[ x_A = 0.604 \]

b) Microfluid

\[ \bar{t} = \frac{C_{A0} - C_A}{-r_A} \]

\[ 1 = \frac{10 - C_A}{9} \]

\[ C_A = 1 \]

\[ x_A = 0.9 \]

As expected, conversion in segregated flow is lower (in this case, considerably lower) than that for a microfluid. Regardless of the degree of micromixing in the reactor, the conversion can never be less than 60.4%.

The absence of a micromixing effect for \(n = 1\) should appear reasonable from another point of view. In a first-order reaction, the probability of an individual reactant molecule undergoing transformation in a given time interval is the same, irrespective of its age and the types and ages of the molecules surrounding it. Consequently, the overall conversion achieved depends only on the residence time distribution of the molecules, and not on how they are dispersed within the reactor.

NOMENCLATURE

\[ C_A = \text{molar concentration of reactant } A \]

\[ \bar{C}_A = \text{mean molar concentration of } A \text{ in the} \]
\[ \text{outflow} \]

\[ C_{A,\text{clump}} = \text{molar concentration of } A \text{ in a fluid element} \]
\[ \text{(clump)} \]

\[ C_{A0} = \text{feed concentration of } A \]

\[ E(t) = \text{residence time density function} \]

\[ k = \text{reaction rate constant} \]

\[ n = \text{reaction order} \]

\[ -r_A = \text{rate of disappearance of reactant } A \]

\[ t = \text{time} \]

\[ \bar{t} = \text{mean residence time} \]

\[ x_A = \text{fractional conversion of } A \]

\[ \tau = \text{reactor space time} \]

LITERATURE CITED


STUDY PROBLEMS

1. Briefly define the following terms:
   a) Clump
   b) Macrofluid
   c) Microfluid
   d) Segregation
   e) Micromixing
   f) Segregated flow model
   g) Maximum mixedness model

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2. A second-order reaction is carried out in an ideal plug flow reactor. Is the reactor performance affected by whether the fluid behaves as a macrofluid or a microfluid? Explain.

3. A second-order reaction is carried out in a perfect mixer.
   a) Is the reactor performance affected by whether the fluid behaves as a macrofluid or a microfluid? If so, how is it affected?
   b) How would the answer change if the reaction was first-order? Half-order?
   c) Does the usual CSTR material balance equation presume macrofluid or microfluid behavior?

4. An ideal CSTR and an ideal PFR are to be convected in series. How should they be connected (CSTR first, PFR first, or order immaterial) to achieve the highest conversion for an nth-order reaction with
   a) \( n = 1/2 \)
   b) \( n = 1 \)
   c) \( n = 3/2 \)

5. An nth-order reaction is carried out in a reactor with a nonideal residence time density function \( E(t) \). Conversion is calculated based on the segregated flow model using Equation 15, but in fact, the reactor is only partially segregated. Is the predicted conversion too high, too low, or correct, for
   a) \( n = 1/2 \)
   b) \( n = 1 \)
   c) \( n = 3/2 \)

6. A continuous fluidized bed reactor is used in ore roasting. A large excess of the reactant gas is used, so that its concentration in the reactor is almost constant. The rate of depletion of the solid reactant is given by:
   \[
   \frac{-dC_s}{dt} = f(C_s, C_f)
   \]
   so that
   \( (C_s/C_o) = F(t, C_f) \)
   for every particle. The mean residence time of the solids in the reactor is \( \bar{\tau} \).
   a) What residence time distribution should one assume for the solids if no tracer data are available?
   b) How would the conversion of solids be calculated?

**HOMEWORK PROBLEMS**

1. Given below are three residence time density functions. For each one, calculate the mean residence time
   \[
   \bar{\tau} = \int_0^\infty tE(t)dt
   \]
   and the expected reactant conversion \( x_s \), assuming
   i) segregated flow; ii) ideal plug flow with the same \( \tau \); iii) perfect mixing (microfluid) with the same \( \tau \).
   When you calculate \( x_s \) based on segregated flow, state whether the calculated value is an upper bound, a lower bound, or an exact estimate of the possible conversions for the given residence time distribution.
   a) For Figure 7,
      \[
      -r_s = 0.1C_s^2 \text{ (mol/L \cdot min)}
      \]
      \( C_{so} = 2 \text{ (mol/L)} \)
   b) For Figure 8,
      \[
      -r_s = 2.5C_s
      \]
      \( C_{so} = 1 \text{ (mol/L)} \)
   c) For Figure 9,
      \[
      -r_s = 0.5C_s^{1.2} \text{ (mol/L \cdot min)}
      \]
      \( C_{so} = 1 \text{ (mol/L)} \)

2. A first-order reaction,
   \[
   A \rightarrow R, -r_s = 0.04C_s \text{ (mol/L \cdot s)}
   \]
   is carried out in an ideal CSTR with a mean residence time of 20 seconds.
   a) How would you expect the conversions for a macrofluid and a microfluid to differ?
   b) Calculate the conversion, assuming segregated flow (Equation 15) and then assuming a
microfluid (the usual CSTR formula). Verify your prediction of Part (a).

3. A second-order reaction,
   \[ A \rightarrow R, \quad -r_A = 0.5 \, C_A^2 \quad \text{(mol/L} \cdot \text{min}) \]
is carried out in an ideal CSTR-PFR series combination. The mean residence time in each reactor is 1 minute, and \( C_{A0} = 5 \) mol/L.

a) Two alternatives are to put the PFR first followed by the CSTR, and vice versa. Would you expect the first alternative to yield a higher conversion, a lower conversion, or the same conversion as the second?

b) Calculate the conversions for both arrangements assuming microfluid behavior, and verify your prediction.

c) Suppose the segregated flow model were used to predict the conversion. Write the integral formula you would use, making all required substitutions but not evaluating the integral. Then give a range for the possible value of \( x_A \) calculated in this manner (e.g. \( x_A < \_ \) or \( x_A \geq \_ \)).

d) Calculate the conversion based on the segregated flow model. Note: values of the exponential integral,
   \[ E_1(z) = \int_{z}^{\infty} \frac{e^{-y}}{y} \, dy \]
are tabulated in a number of reference handbooks, such as that of Abramowitz and Stegun (4). One such value is \( E_1(1.4) = 0.116219 \).

4. A first-order reaction (\( k = 0.1 \text{ min}^{-1} \)) is carried out in a flow reactor. A tracer response test is used to determine the residence time density function in the reactor, with the results given in Table 3. Verify that the \( E(t) \) curve is normalized. Then calculate the mean residence time and the expected conversion, using Simpson's rule for all required integrations. Finally, calculate the conversion that would be achieved in an ideal PFR and a perfect mixer with the same mean residence time.

<table>
<thead>
<tr>
<th>Table 3.</th>
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<td>( t (\text{min}) )</td>
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<td>( E(t) (\text{min}^{-1}) )</td>
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SOLUTIONS TO THE STUDY PROBLEMS

1. (a) **Clump:** a collection of molecules small enough to occupy no more than a microscopic volume in a reactor, but large enough for the concept of concentration to be meaningful.

(b) **Macrofluid:** molecules are organized in coherent clumps. All molecules in a clump have the same age.

(c) **Microfluid:** molecules are randomly dispersed, irrespective of age.

(d) **Segregation:** The tendency of the contents of a reactor to behave as a macrofluid.

(e) **Macromixing:** the phenomenon whereby residence times of clumps are distributed about a mean value.

(f) **Micromixing:** mixing among molecules of different ages. (Put another way, mixing between macrofluid clumps.)

(g) **Segregated flow model:** the fluid in a flow reactor is assumed to behave as a macrofluid. Each clump functions as a miniature batch reactor. Mixing of molecules of different ages occurs as late as possible.

(h) **Maximum mixedness model:** the fluid in a flow reactor behaves as a microfluid. Mixing of molecules of different ages occurs as early as possible.

2. **No.** Every molecule in an ideal PFR is surrounded by other molecules with the same age, so that all adjacent clumps have the same composition. Whether or not there is exchange between clumps is immaterial.

3. (a) **Yes. Conversion is higher for the macrofluid.**

(b) **1st - order:** No difference.

(c) **½ - order:** Conversion is higher for the microfluid.

(c) **Microfluid.**
4. (a) CSTR-PFR
   (b) No difference
   (c) PFR-CSTR

5. (a) Too low
   (b) Correct
   (c) Too high

6. (a) \[ E(t) = \frac{1}{\bar{\tau}} \exp\left(-t/\bar{\tau}\right) \]
   (b) Use the segregated flow model [Eq. (15)]. Using the usual CSTR equation would be equivalent to assuming that the solids behave as a microfluid, which is certainly not the case.