

3. RESIDENCE TIME DISTRIBUTION AND REACTOR PERFORMANCE

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:

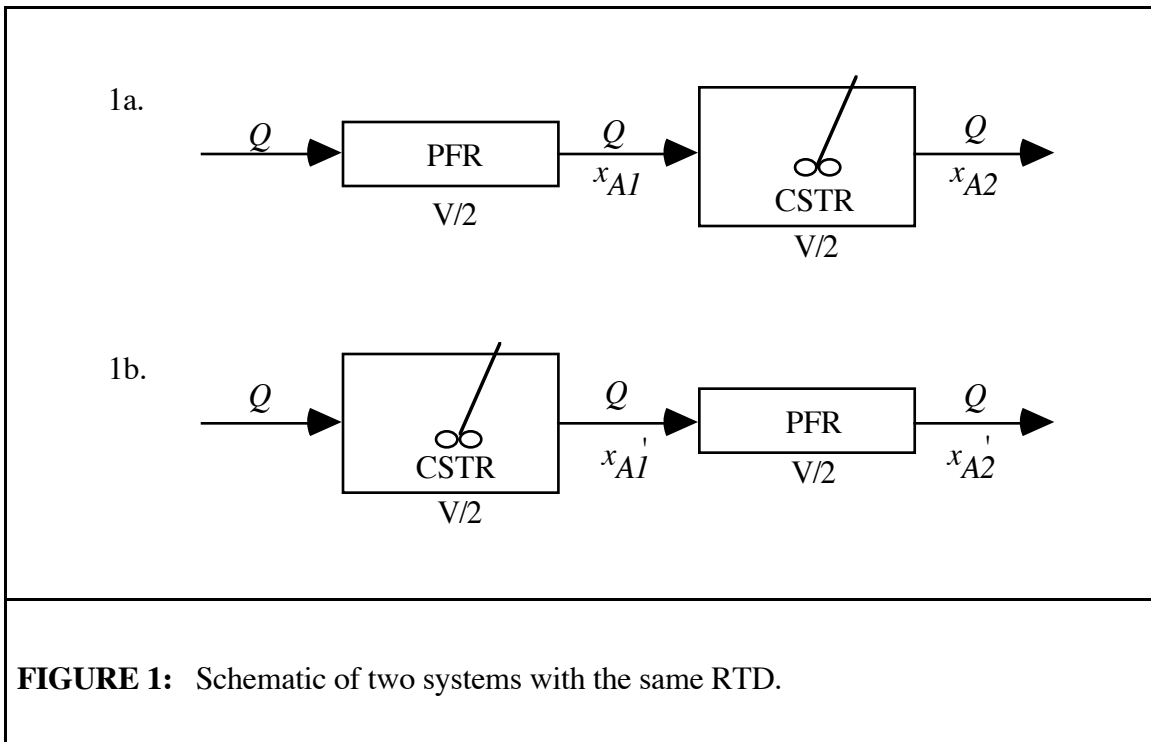


FIGURE 1: Schematic of two systems with the same RTD.

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

$$E(t) = \frac{2}{\bar{t}} e^{-\frac{2(t-\bar{t}/2)}{\bar{t}}} H\left(t - \frac{\bar{t}}{2}\right); \quad \bar{E}(s) = \frac{e^{-\frac{\bar{t}}{2}s}}{1 + \frac{\bar{t}}{2}s}$$

where $H(t - a) = \begin{cases} 0 & t < a \\ 1 & t > a \end{cases}$ is the Heaviside's unit step function.

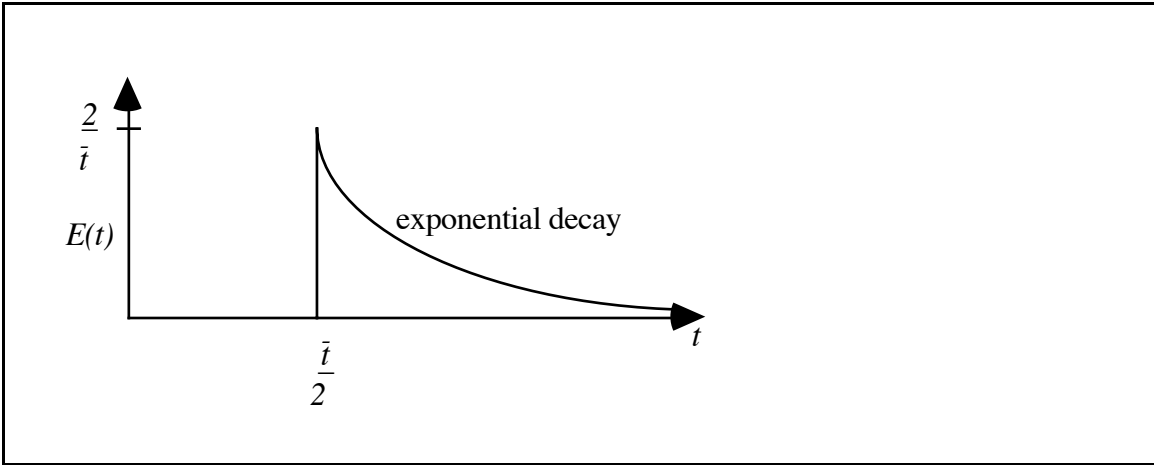
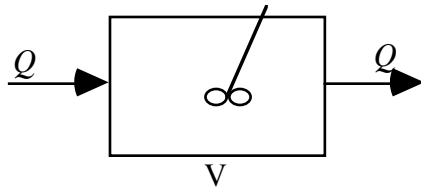


FIGURE 2: Impulse response of both systems 1a and 1b.

EXAMPLE 2:

2a.



2b.

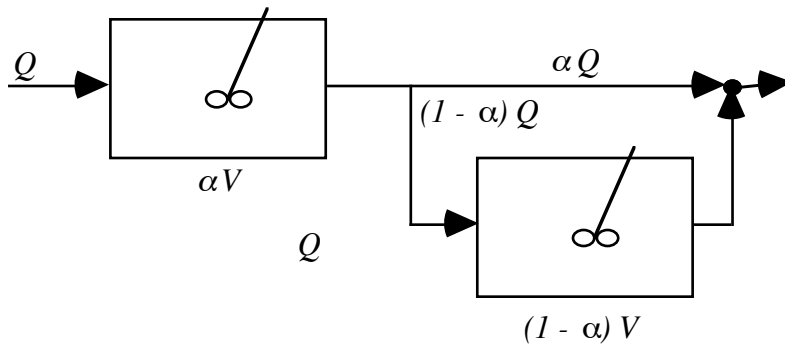
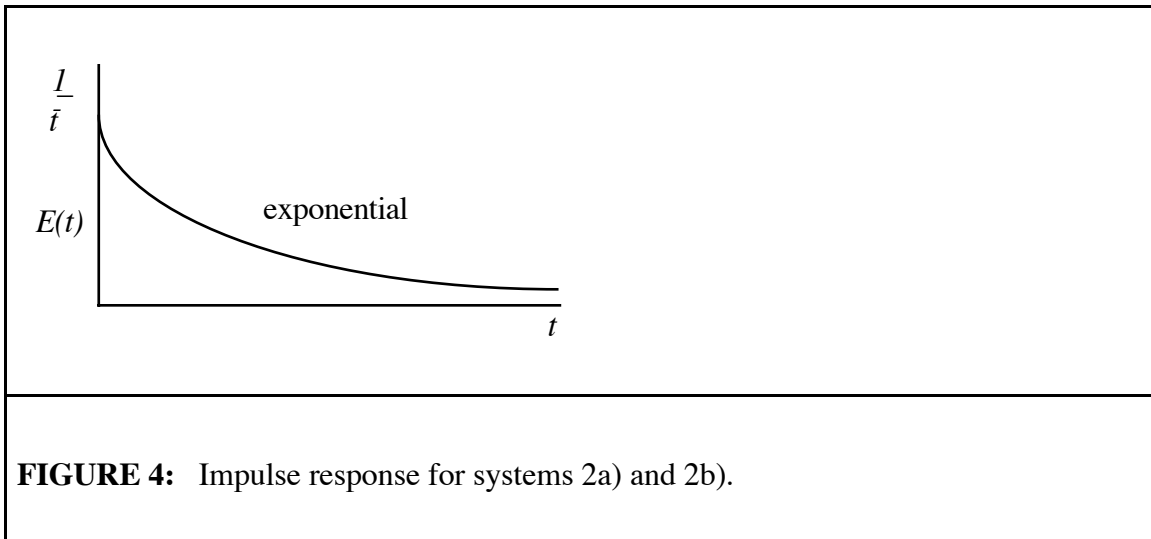


FIGURE 3: Schematic of two flow systems with the exponential E curve.

The E-curve for both systems 2a and 2b is:

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

$$\bar{E}(s) = \frac{1}{1 + \bar{t}s}$$



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:

$$\text{First reactor PFR:} \quad \frac{\bar{t}}{2} = \int_{C_{A1}}^{C_{A0}} \frac{dC_A}{kC_A} = \frac{1}{k} \ln \frac{C_{A0}}{C_{A1}}$$

$$\text{Second reactor CSTR:} \quad \frac{\bar{t}}{2} = \frac{C_{A1} - C_{A2}}{kC_{A2}}$$

$$\text{Hence, } 1 - x_{A2} = \frac{C_{A2}}{C_{A0}} = \frac{e^{-k\bar{t}/2}}{1 + \frac{k\bar{t}}{2}}$$

SYSTEM 1b:

$$\text{First reactor CSTR:} \quad \frac{\bar{t}}{2} = \frac{C_{A0} - C_{A1}'}{kC_{A1}'}$$

$$\text{Second reactor PFR:} \quad \frac{\bar{t}}{2} = \int_{C_{A2}'}^{C_{A1}'} \frac{dC_A}{kC_A} = \frac{1}{k} \ln \frac{C_{A1}'}{C_{A2}'}$$

$$1 - x_{A2}' = \frac{C_{A2}'}{C_{A0}} = \frac{e^{-k\bar{t}/2}}{1 + k\bar{t}/2}$$

$$x_{A2} = x_{A2}' = 1 - \frac{e^{-Da/2}}{1 + Da/2} \quad \text{where } Da = Da_1 = k\bar{t}$$

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:

$$\text{First reactor PFR:} \quad \frac{\bar{t}}{2} = \int_{C_{A1}}^{C_{A0}} \frac{dC_A}{kC_A^2} = \frac{1}{k} \left(\frac{1}{C_{A1}} - \frac{1}{C_{A0}} \right)$$

$$\text{Second reactor CSTR: } \frac{\bar{t}}{2} = \frac{C_{A1} - C_{A2}}{kC_{A2}^2}$$

$$1 - x_{A2} = \frac{C_{A2}}{C_{A0}} = \frac{\sqrt{1 + \frac{2k\bar{t}C_{A0}}{1 + k\frac{\bar{t}}{2}C_{A0}} - 1}}{k\bar{t}C_{A0}}$$

SYSTEM 1b:

$$\text{First reactor CSTR: } \frac{\bar{t}}{2} = \frac{C_{A0} - C_{A1}'}{kC_{A1}'^2}$$

$$\text{Second reactor PFR: } \frac{\bar{t}}{2} = \frac{1}{k} \left(\frac{1}{C_{A2}'} - \frac{1}{C_{A1}'} \right)$$

$$1 - x_{A2}' = \frac{C_{A2}'}{C_{A0}} = \frac{\sqrt{1 + 2k\bar{t}C_{A0}} - 1}{\frac{k\bar{t}}{2} [2 + \sqrt{1 + 2k\bar{t}C_{A0}} - 1]}$$

Note that both expressions for conversion are a function of the Damkohler number for the system, where $Da = Da_2 = k\bar{t}C_{A0}$.

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

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

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

Da	x_{A2}	x_{A2}'
1	0.472	0.464
2	0.634	0.618
4	0.771	0.750

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

$$x_{A2} = \frac{Da}{2} - \frac{3Da^2}{16} + \frac{Da}{2} \sqrt{1 - \frac{Da}{2} + \frac{Da^2}{8}} \quad \text{for system 1a}$$

$$x'_{A2} = Da \sqrt{1 + \frac{Da^2}{16}} - \frac{5Da^2}{16} \quad \text{for system 1b}$$

Da	x_{A2}	x'_{A2}
0.5	0.424	0.426
1	0.708	0.718
2	0.957	0.986

You should check the above expressions and draw your own conclusions by plotting x_{A2} and x'_{A2} vs $Da = Da_{1/2} = k\bar{t} / C_{Ao}^{1/2}$.

Let us now consider system 2 and a 1st order irreversible reaction.

SYSTEM 2a:

$$x_{A_2} = \frac{Da}{1 + Da}$$

SYSTEM 2b:

$$C_{A_1} = \frac{C_{Ao}}{1 + \alpha k \bar{t}} \text{ is the exit reactant concentration from the 1st CSTR.}$$

$$C_{A_2} = \frac{C_{A_1}}{1 + k\bar{t}} = \frac{C_{Ao}}{(1 + k\bar{t})(1 + \alpha k\bar{t})} \text{ is the exit reactant concentration from the 2nd CSTR.}$$

The balance around the mixing point where the two streams join yields:

$$C_{A_b} = \alpha C_{A_1} + (1 - \alpha) C_{A_2} = C_{A_o} \left[\frac{\alpha}{1 + \alpha k\bar{t}} + \frac{1 - \alpha}{(1 + k\bar{t})(1 + \alpha k\bar{t})} \right] =$$
$$\frac{C_{A_o} (\alpha + \alpha k\bar{t} + 1 - \alpha)}{(1 + \alpha k\bar{t})(1 + k\bar{t})} = \frac{C_{A_o}}{1 + k\bar{t}} = \frac{C_{A_o}}{1 + Da}$$

Hence,

$$x_{A_b} = 1 - \frac{C_{A_b}}{C_{A_o}} = \frac{Da}{1 + Da}$$

$$x_{A_a} = x_{A_b}$$

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

$$L_i(t) dt = (\text{fraction of the elements of the inflow with life expectancy between } t \text{ \& } t + dt) \quad (54)$$

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

$$L_i(t) = E(t) \quad (55)$$

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:

$$C_{A_{out}} = \sum_{all t_i} \left(\begin{array}{l} \text{reactant concentration} \\ \text{after batch reaction time } t_i \end{array} \right) \times \left(\begin{array}{l} \text{fraction of the outflow} \\ \text{of residence time around } t_i \end{array} \right)$$

$$C_{A_{out}} = \lim_{\substack{\Delta t_i \rightarrow 0 \\ N \rightarrow \infty}} \sum_{i=1}^N C_{A_{batch}}(t_i) E(t_i) \Delta t_i$$

$$C_{A_{out}} = \int_0^{\infty} C_{A_{batch}}(\tau) E(\tau) d\tau \quad (56)$$

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

$$-\frac{dC_{A_{batch}}}{d\tau} = kC_{A_{batch}}^n; \text{ at } \tau = 0; C_{A_{batch}}(0) = C_{A_0} \quad (57)$$

Now for a 1st order irreversible reaction:

$$C_{A_{batch}}(\tau) = C_{A_0} e^{-k\tau} \quad (58)$$

so that

$$C_{A_{out}} = C_{A_0} \int_0^{\infty} e^{-k\tau} E(\tau) d\tau \quad (56a)$$

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:

$$x_A = 1 - \frac{C_{A_{out}}}{C_{A_0}} = 1 - \int_0^{\infty} e^{-k\tau} E(\tau) d\tau = 1 - \bar{E}(s)|_{s=k} \quad (56b)$$

Using the above formula we get:

$$\text{For system 1: } x_A = 1 - \frac{e^{-k\bar{t}/2}}{1 + k\bar{t}/2} = 1 - \frac{e^{-Da/2}}{1 + Da/2} \quad (59a)$$

$$\text{For system 2: } x_A = 1 - \frac{1}{1 + k\bar{t}} = \frac{k\bar{t}}{1 + k\bar{t}} = \frac{Da}{1 + Da} \quad (59b)$$

In terms of dimensionless quantities, $\bar{t} E(t) = E_{\theta}(\theta)$, and for a first order reaction we can write:

$$x_A = 1 - \int_0^{\infty} e^{-Da\theta} E_{\theta}(\theta) d\theta = 1 - \bar{E}_{\theta}(s)|_{s=Da} \quad (56c)$$

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:

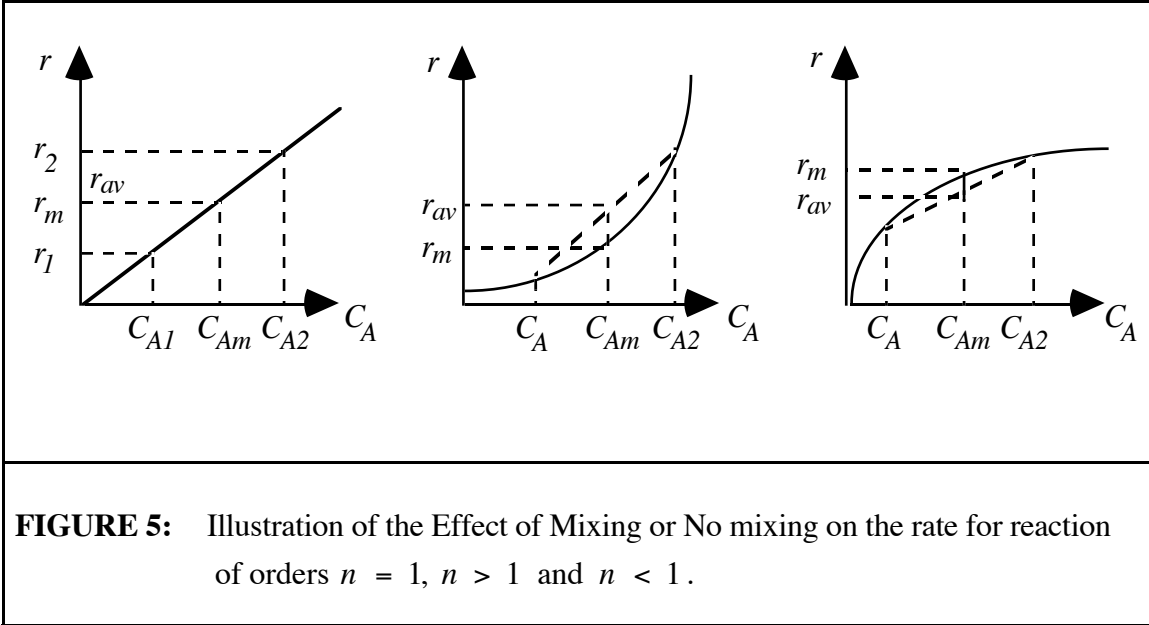
$$x_A = \int_0^{\infty} x_{A_{batch}}(\theta) E(\theta) d\theta \quad (60)$$

Where for n-th order irreversible kinetics

$$\frac{dx_{A_{batch}}}{d\theta} = Da_n (1 - x_A)^n; \quad \theta = 0, x_A = 0 \quad (61)$$

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 θ 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:

$$r_m = r\left(\frac{C_{A_1} + C_{A_2}}{2}\right) \quad r_{av} = \frac{r(C_{A_1}) + r(C_{A_2})}{2} \quad (62)$$



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_{A1}, r_1) and (C_{A2}, 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 abscissa 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 $\frac{d^2r}{dC_A^2} \equiv 0$ 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:

$$x_A = \int_0^\infty x_{A_{batch}}(\theta) 2e^{-2\left(\theta - \frac{1}{2}\right)} H\left(\theta - \frac{1}{2}\right) d\theta \quad (63)$$

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

So that upon integration we get

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

Substituting this into the above equation (63) yields:

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

Upon substitution in the second integral of

$$x = \frac{2}{Da} (1 + Da\theta) \quad (67)$$

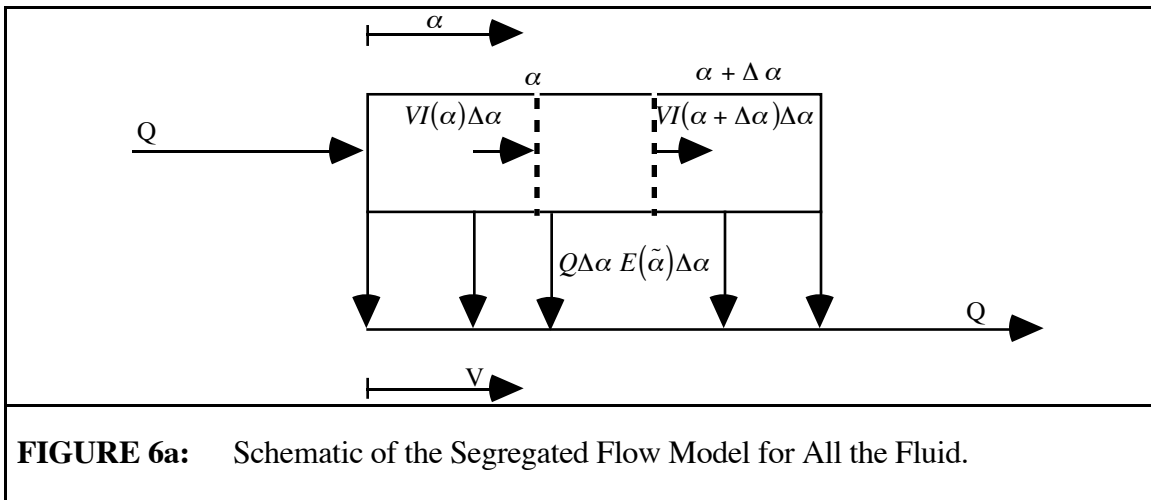
we get

$$x_A = 1 - \frac{2}{Da} e^{\left(1 + \frac{2}{Da}\right)} \int_{1 + \frac{2}{Da}}^{\infty} \frac{e^{-x}}{x} dx \quad (68)$$

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. Its 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 α_p is the mean age for the point under consideration.

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



An element of volume of the system occupied by fluid elements of age between α 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 α and $\alpha + \Delta\alpha$, i.e. in the differential volume, $dV = VI(\alpha)d\alpha$ as sketched in the figure.

We can write:

$$\begin{aligned} & \text{(Elements in the reactor of age about } \alpha + \Delta\alpha) = \\ & \text{(Elements in the reactor of age about } \alpha) - \\ & \text{(Elements of the outflow of age about } \tilde{\alpha} \text{ collected during time interval } \Delta\alpha) \end{aligned}$$

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

$$VI(\alpha + \Delta\alpha)\Delta\alpha = VI(\alpha)\Delta\alpha - \int_{\alpha}^{\alpha + \Delta\alpha} Q \left[\int_{\alpha}^{\alpha + \Delta\alpha} E(\alpha) d\alpha \right] d\alpha \quad (69)$$

Using the mean value theorem we get:

$$\begin{aligned} VI(\alpha + \Delta\alpha)\Delta\alpha - VI(\alpha)\Delta\alpha &= -Q\Delta\alpha E(\tilde{\alpha})\Delta\alpha \\ \alpha &\leq \tilde{\alpha} \leq \alpha + \Delta\alpha \end{aligned}$$

Taking the limit as $\Delta\alpha \rightarrow 0$ yields

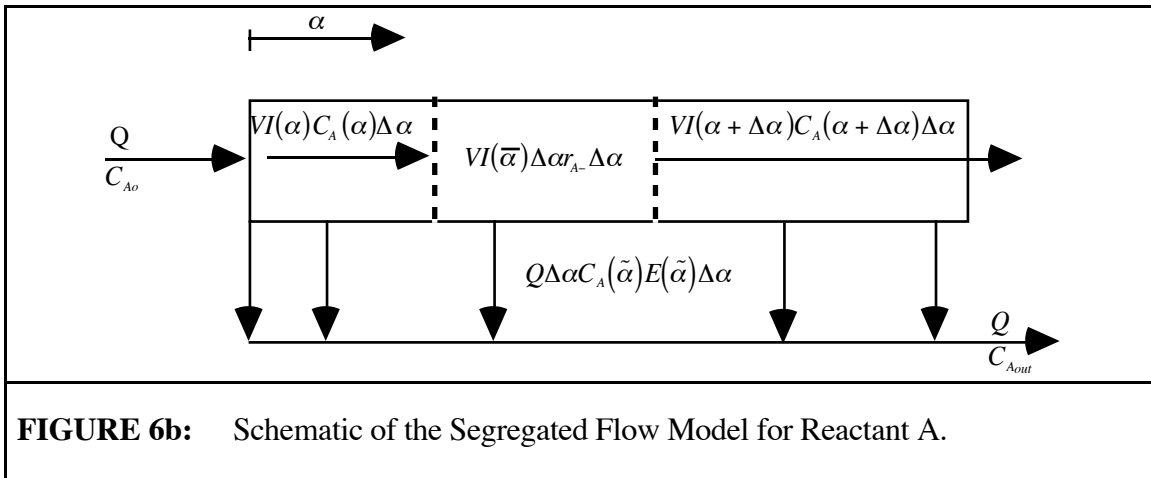
$$\frac{V}{Q} \lim_{\Delta\alpha \rightarrow 0} \frac{I(\alpha + \Delta\alpha) - I(\alpha)}{\Delta\alpha} = - \lim_{\Delta\alpha \rightarrow 0} E(\tilde{\alpha}) \quad (69)$$

$$\bar{t} \frac{dI}{d\alpha} = -E(\alpha) \quad (70)$$

$$\alpha = \infty \quad I = 0 \quad (70a)$$

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 α and $\alpha + \Delta\alpha$.



(Reactant elements in the reactor of age about $\alpha + \Delta\alpha$) =

(Reactant elements in the reactor of age about α) -

(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 $\Delta\alpha$).

$$\begin{aligned} VI(\alpha + \Delta\alpha) C_A(\alpha + \Delta\alpha) \Delta\alpha &= VI(\alpha) C_A(\alpha) \Delta\alpha \\ -Q\Delta\alpha E(\tilde{\alpha}) C_A(\tilde{\alpha}) \Delta\alpha &- VI(\tilde{\alpha}) \Delta\alpha r_{A-} (C_A(\tilde{\alpha})) \Delta\alpha \end{aligned} \quad (71)$$

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 $\Delta\alpha \rightarrow 0$ we get:

$$\begin{aligned} \bar{t} \lim_{\Delta\alpha \rightarrow 0} \frac{I(\alpha + \Delta\alpha) C_A(\alpha + \Delta\alpha) - I(\alpha) C_A(\alpha)}{\Delta\alpha} &= \\ - \lim_{\Delta\alpha \rightarrow 0} \left\{ E(\tilde{\alpha}) C_A(\tilde{\alpha}) \right\} &- \bar{t} \lim_{\Delta\alpha \rightarrow 0} \left\{ I(\tilde{\alpha}) r_{A-} (C_A(\tilde{\alpha})) \right\} \end{aligned} \quad (72)$$

$$\begin{aligned} \bar{t} \frac{d}{d\alpha} (IC_A) &= -EC_A - \bar{t}r_{A-} \\ \bar{t} \frac{dI}{d\alpha} C_A + \bar{t}I \frac{dC_A}{d\alpha} &= -EC_A - \bar{t}r_{A-} \\ -EC_A + \bar{t}I \frac{dC_A}{d\alpha} &= -EC_A - \bar{t}r_{A-} \\ \bar{t}I \left[\frac{dC_A}{d\alpha} + r_{A-} \right] &= 0 \end{aligned} \quad (73)$$

This is satisfied for all α only if

$$\frac{dC_A}{d\alpha} + r_{A-} = 0 \quad (74)$$

Reorganizing this we get:

$$\left. \begin{aligned} - \frac{dC_A}{d\alpha} &= r_{A-} \\ \alpha = 0, \quad C_A &= C_{A0} \end{aligned} \right\} \quad (75)$$

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).

$$C_{A_{out}} = \int_0^{\infty} C_A(\alpha) E(\alpha) d\alpha \quad (76)$$

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

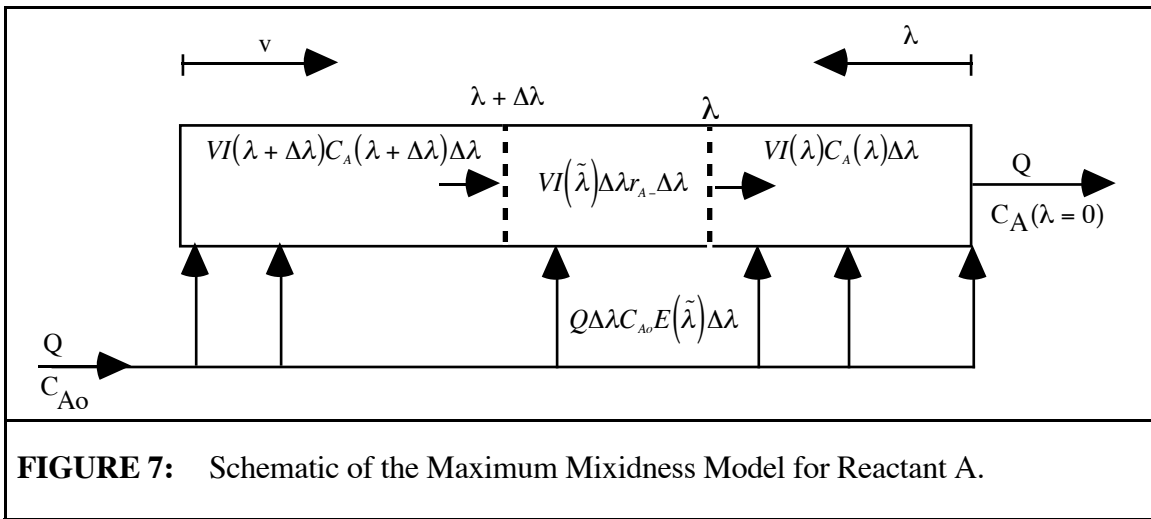
Besides classifying the fluid elements according to their age, one can also group them according to their life expectation, where life expectancy is the time that will elapse between the time of observation of the system and the moment when the fluid element leaves the system. In this manner each fluid 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 $L_t(t) = E(t)$. 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 λ , $VL_s(\lambda) d\lambda$, must equal the number of elements of age $\alpha = \lambda$, $VI(\lambda) d\lambda$, 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 expectancy $\lambda = 0$ 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. 11, 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 λ_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.



The life expectancy 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 λ 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 expectancy and are mixing it with the fluid of other ages but with the same life expectancy.

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

(Elements of the system with life expectancy about λ) =

(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 $\lambda \leq \tilde{\lambda} \leq \lambda + \Delta\lambda$.

$$\text{Then } VI(\lambda)\Delta\lambda = VI(\lambda + \Delta\lambda)\Delta\lambda + Q\Delta\lambda E(\tilde{\lambda})\Delta\lambda \quad (77)$$

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

$$-\bar{t} \lim_{\Delta\lambda \rightarrow 0} \frac{I(\lambda + \Delta\lambda) - I(\lambda)}{\Delta\lambda} = \lim_{\Delta\lambda \rightarrow 0} E(\tilde{\lambda})$$

$$-\bar{t} \frac{dI}{d\lambda} = E(\lambda) \quad (78)$$

$$\lambda \rightarrow \infty \quad I = 0 \quad (78a)$$

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** λ and $\lambda + \Delta\lambda$ (Refer to Figure 7).

(Reactant elements in the system of life expectancy about λ) =

(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 $\Delta\lambda$)

$$VI(\lambda)\Delta\lambda C_A(\lambda) = VI(\lambda + \Delta\lambda) C_A(\lambda + \Delta\lambda)\Delta\lambda$$

$$+ Q\Delta\lambda E(\tilde{\lambda})\Delta\lambda C_{A_0} - VI(\tilde{\lambda})\Delta\lambda r_{A-}(C_A(\tilde{\lambda}))\Delta\lambda \quad (79)$$

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

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

$$C_{A_0} \lim_{\Delta\lambda \rightarrow 0} E(\tilde{\lambda}) - \bar{t} \lim_{\Delta\lambda \rightarrow 0} I(\tilde{\lambda}) r_{A-}(C_A(\tilde{\lambda}))$$

$$\underbrace{-\bar{t} \frac{d(IC_A)}{d\lambda}} = C_{A_0} E - \bar{t} I r_{A-}$$

$$\underbrace{-\bar{t} \frac{dI}{d\lambda} C_A - \bar{t} I \frac{dC_A}{d\lambda}}_E = C_{A_0} E - \bar{t} I r_{A-}$$

$$E C_A - \bar{t} I \frac{dC_A}{d\lambda} = C_{A_0} E - \bar{t} I r_{A-}$$

$$\frac{dC_A}{d\lambda} + \frac{E}{\bar{t} I} (C_{A_0} - C_A) - r_{A-} = 0 \quad (80)$$

or

$$\frac{dC_A}{d\lambda} = r_{A-} - \frac{E(\lambda)}{W(\lambda)} (C_{A_0} - C_A) \quad (80a)$$

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

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

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

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

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 λ the value of $\frac{dC_A}{d\lambda}$ is almost zero.

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

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

or

$$(b) \quad x = \frac{1}{1 + \lambda}; \quad \lambda = \frac{1-x}{x} \quad (82b)$$

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 $\frac{d^2r}{dC_A} > 0$ and upper bound on conversion for monotonic rates with $\frac{d^2r}{dC_A^2} < 0$.

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:

$$\lambda_k \approx \left(\frac{v^3}{\dot{\epsilon}} \right)^{1/4} \quad (83)$$

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

$$\tau_D = \frac{\lambda_k^2}{D} = \frac{(10^{-3})^2}{10^{-5}} = 10^{-1} s \quad (84)$$

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

$$\bar{t} = \frac{C_{A0} - C_{A\infty}}{r_{A-}(C_{A\infty})} \quad (85)$$

However, since $E(\lambda)/W(\lambda) = \frac{1}{\bar{t}}$ is independent of λ , eq (80a) is satisfied by eq (85) for all λ . Therefore $C_A(\lambda = 0) = C_{A\infty}$ 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:

$$C_A = \frac{1}{\bar{t}} \int_0^{\infty} e^{-t/\bar{t}} C_{A_{batch}}(t) dt = \int_0^{\infty} e^{-\theta} C_{A_{batch}}(\theta) d\theta \quad (86)$$

and the maximum mixedness model gives

$$\bar{t} = \frac{C_{A0} - C_A}{r_{A-}(C_A)} \quad (87)$$

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

$$C_A = \int_0^{\infty} \delta(t - \bar{t}) C_{A_{batch}}(t) dt = C_{A_{batch}}(\bar{t}) \quad (88)$$

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 $\delta(t - \bar{t})(C_{A0} - C_A)$ in eq (80a), by

$$\lambda = \bar{t}, C_A = C_{A0} \quad (89)$$

Then eq (80a) becomes

$$\frac{dC_A}{d\lambda} = r_{A-} \quad (90)$$

If we substitute $t = \bar{t} - \lambda$ the maximum mixedness PFR equation becomes

$$\frac{dC_A}{dt} = -r_A \quad (91)$$

$$t = 0 \quad C_A = C_{A_0} \quad (92)$$

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

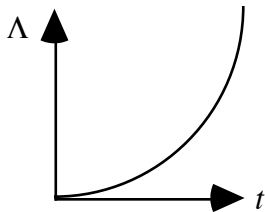
$$C_A = \int_0^{\infty} C_{A_0} e^{-kt} E(t) dt \quad (93)$$

and the maximum mixedness model

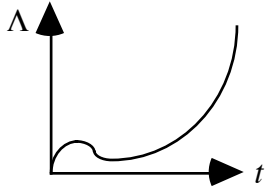
$$\frac{dC_A}{d\lambda} = kC_A - \frac{E(\lambda)}{W(\lambda)} (C_{A_0} - C_A) \quad (94)$$

$$\lambda \rightarrow \infty \quad \frac{dC_A}{d\lambda} = 0 \quad (95)$$

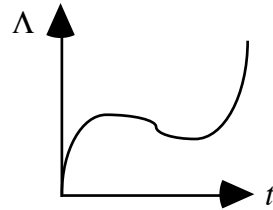
One should note that the function appearing in the above formulation of the maximum mixedness model, i.e. E/W has special significance, is called the intensity function and is very useful in evaluation of stagnancy or bypassing within the system as described in the previous section.



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.

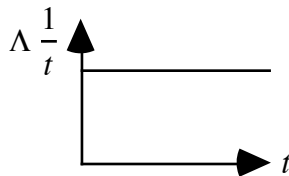


Bypassing. Some fluid has increased probability of leaving at a very young age. Rest of the fluid behaves normally.

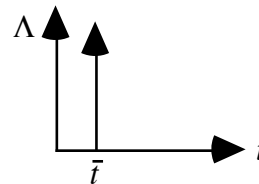


Stagnancy. After main flow leaves the probability of the fluid caught in dead zones to exit decreases until very large ages are reached at which point all fluid must ultimately leave.

For a CSTR



For a PFR



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:

1. Danckwerts, P.V., Chem. Eng. Science, **2**, 1 (1953)
2. Danckwerts, P.V., Chem. Eng. Science, **8**, 93 (1953)
3. Zwietering, T.W., Chem. Eng. Science, **77**, 1 (1959)