

Process Fundamentals

Chemical, biological and physical reaction in engineered systems usually take place in "reactors". Reactors represent some sort of containment that physically define the processes. It is important to know the mixing level and residence time in reactors since both affect the degree of process reaction that occurs while the fluid (usually water) and its components pass through the reactor.

Reactor Classification:

Mixing levels give rise to three categories of reactors:

- completely mixed flow (CMF)
- plug flow (PF)
- flow with dispersion (FD).

The first two are idealized extremes not attainable in practice, but serve as convenient mathematical models.

All **real** reactors fall under the category of FD.

Fluid Transport

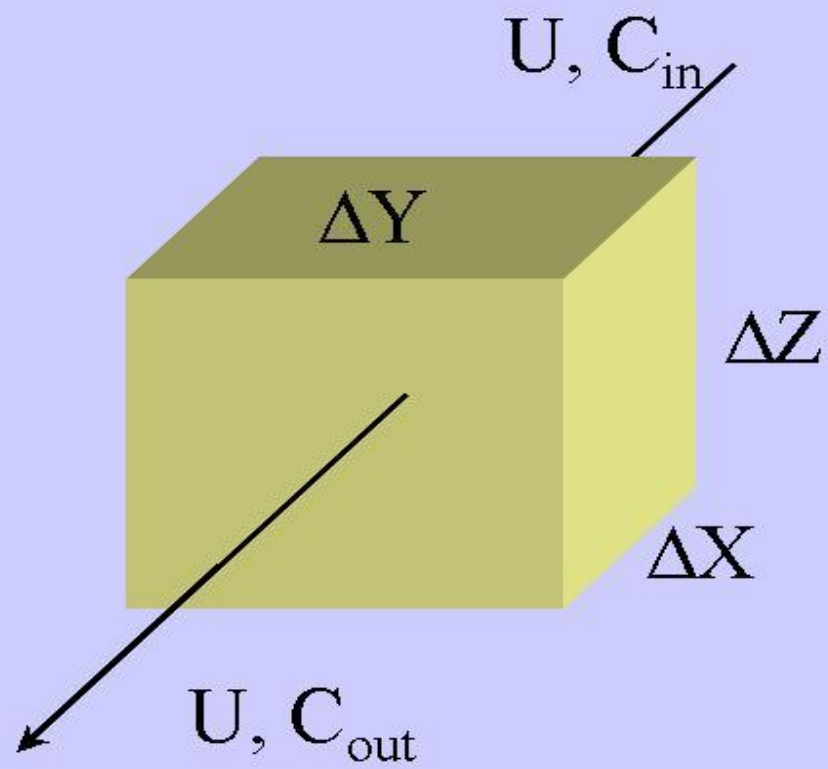
Depending on the level of mixing, fluid transport of contaminants (pollutants) can be by:

- Advection
- Molecular Diffusion
- Turbulent Diffusion
- Shear Flow Dispersion

ADVECTION

Advection is movement of the contaminant with the fluid (concurrently).

Consider a conservative material, in the absence of any diffusive mechanisms, moving in one direction, say the x-direction. The absence of any diffusive activity means that the pollutant remains associated with the same water “packet” with which it was initially associated.



If we do a mass balance on an elemental volume:
Mass flow in – mass flow out = time rate of
accumulation in the elemental volume.

Let Q = flow rate = $u(\Delta z)(\Delta y)$.

Where u = fluid flow rate (m/sec).

Then:

$$C_{\text{in}} \cdot Q - C_{\text{out}} \cdot Q = \frac{\Delta C_{\text{vol}}}{\Delta t} \cdot \Delta x \cdot \Delta y \cdot \Delta z$$

$$\frac{(C_{\text{in}} - C_{\text{out}}) \cdot Q}{\Delta x \cdot \Delta y \cdot \Delta z} = (C_{\text{in}} - C_{\text{out}}) \cdot \frac{u}{\Delta x}$$

Let $(C_{\text{out}} - C_{\text{in}}) = \Delta C$

Then,

$$\frac{\Delta C_{\text{vol}}}{\Delta t} = -u \cdot \frac{\Delta C}{\Delta x}$$

In the limit, the size of the elemental volume can be set infinitely small so that:

$$\Delta C_{\text{vol}} \rightarrow \partial C$$

$$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial x}$$

In three dimensions:

$$-\frac{\partial C}{\partial t} = u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} + w \frac{\partial C}{\partial z}$$

MOLECULAR DIFFUSION

In the absence of bulk fluid motion we can still get net mass transport via diffusive phenomena. First look at molecular diffusion .

In typical treatment processes molecular diffusion is overwhelmed by turbulence (another type of diffusive transport property). But at interfaces (water- air and water-solid) molecular diffusion can become important. In addition, we can use the same mathematical model as we use to describe molecular diffusion for general diffusion processes.

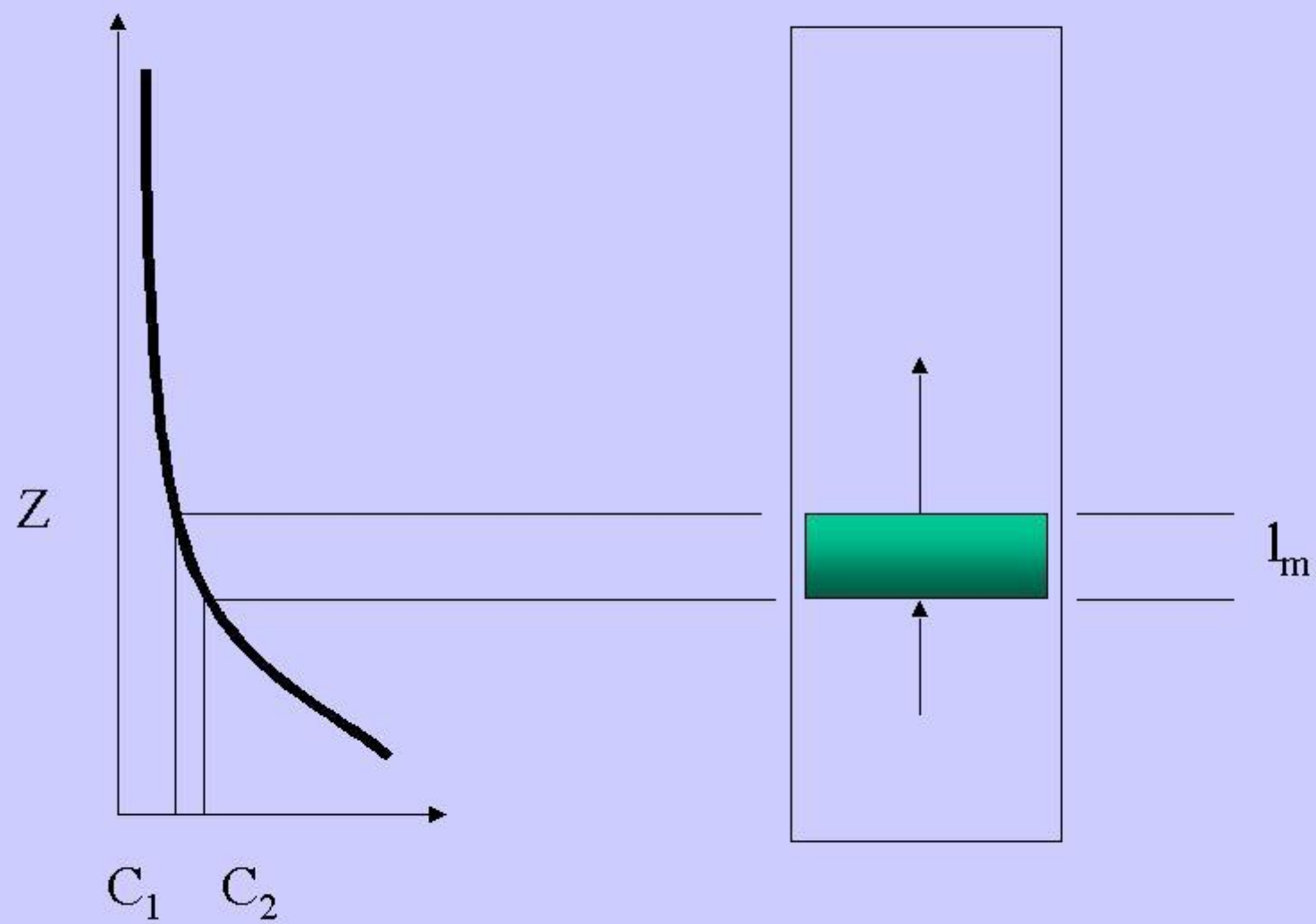
Molecular diffusion is a phenomenon caused by kinetic energy of molecules and by concentration gradients. Molecules undergo random motion which is caused by internal energy of the molecules. Each molecule possesses at least three types of energy.

- 1) translational (only significant one in the diffusion process)
- 2) rotational
- 3) vibrational

As long as there are no concentration gradients motion is random and there is no internal flux in the system. Collisions of particles (molecules) will occur randomly resulting in random changes in particle motion and position.

Mathematical Model (Fick's Law)

Consider the situation where a concentration gradient exists (by some set of initial conditions). Molecular collisions will now be less frequent in the direction of lower molecular concentration. Therefore, there will be a net movement (flux) of molecules from high to low concentration regions as shown in the figure below.



Groups of molecules move at velocity of w_m (in the z direction). Define l_m as the average distance molecules (or particles) travel before they collide with other particles. This is called the **mean free path**. Of course, the mean free path and the average velocity are function of the concentration of molecules. But for dilute solutions we can assume that they are constant at a constant temperature. The net mass flux into the shaded region is given by (on a unit area basis):

$$J_z = C_{in} \cdot w_m - C_{out} \cdot w_m$$
$$= w_m \cdot (C_{in} - C_{out})$$

J (flux) has typical units of mass/m²-sec
C usually has units of mass/volume.

If the distance and concentration are small enough:

$$\frac{C_{\text{out}} - C_{\text{in}}}{l_{\text{m}}} \approx \frac{\partial C}{\partial z}$$

$$l_{\text{m}} \cdot \frac{\partial C}{\partial z} \approx C_{\text{out}} - C_{\text{in}}$$

(second order terms in Taylor expansion are approximately zero if the distance and the concentration gradient are small). So that:

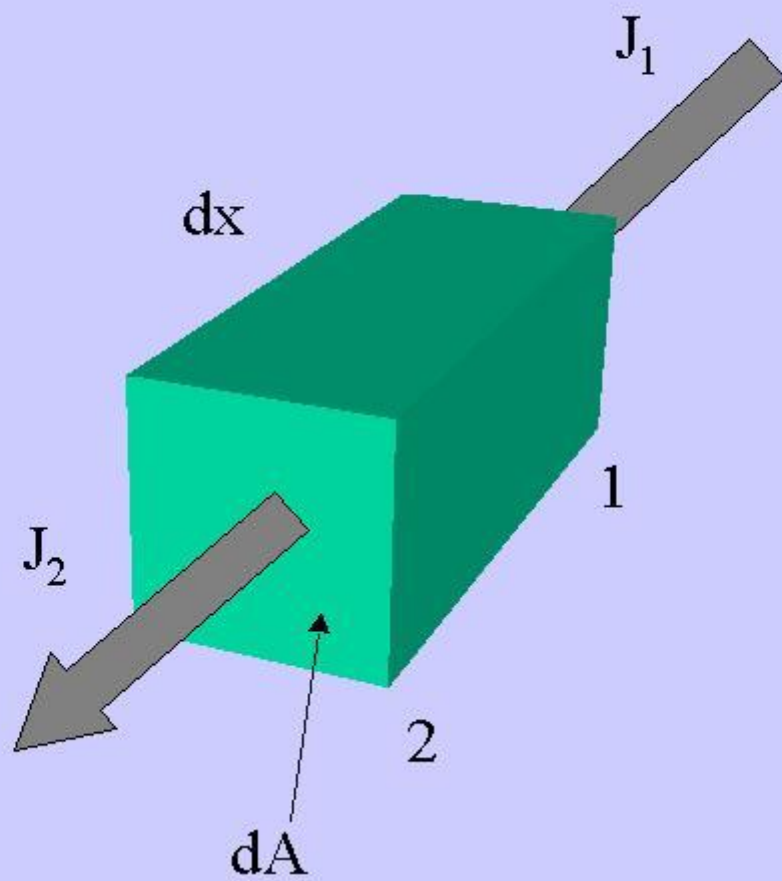
$$J_z = -w_m l_m \frac{\partial C}{\partial z}$$

The product $w_m l_m = D$ (**coefficient of molecular diffusivity**). D has typical units of cm^2/sec . D is a function of temperature, solvent and molecule type and size.

In three dimensions (assuming uniform D):

$$J = -D \frac{\partial C}{\partial x} - D \frac{\partial C}{\partial y} - D \frac{\partial C}{\partial z}$$

Now look at transport with just molecular diffusion , i.e., assume no advection. Again a mass balance can be performed on an elemental volume for a conservative material. Again assume that diffusion occurs in only the x-direction (both positive and negative).



$$J_1 = -D \left(\frac{\partial C}{\partial x} \right)_1$$

$$J_2 = -D \left(\frac{\partial C}{\partial x} \right)_2$$

Again using in – out = mass rate of accumulation in the elemental volume gives:

$$dA \left\{ -D \left(\frac{\partial C}{\partial x} \right)_1 - \left[-D \left(\frac{\partial C}{\partial x} \right)_2 \right] \right\} = \frac{dM}{dt}$$

mathematically:

$$\left(\frac{\partial C}{\partial x}\right)_2 = \left(\frac{\partial C}{\partial x}\right)_1 + \frac{\partial}{\partial x} \left(\frac{\partial C}{\partial x}\right) \cdot dx$$

After dividing through by dA:

$$D \left(\frac{\partial C}{\partial x}\right)_2 - D \left(\frac{\partial C}{\partial x}\right)_1 = D \frac{\partial}{\partial x} \left(\frac{\partial C}{\partial x}\right) dx = \frac{\partial M}{dA dt}$$

$$D \frac{\partial}{\partial x} \left(\frac{\partial C}{\partial x} \right) = D \left(\frac{\partial^2 C}{\partial x^2} \right) = \frac{1}{dA} \frac{dM}{dxdt} = \frac{dC}{dt}$$

$$\frac{dM}{dXdA} = dC$$

This results in Fick's Second law in 1 dimension and 3 dimensions, respectively:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + D \frac{\partial^2 C}{\partial y^2} + D \frac{\partial^2 C}{\partial z^2}$$

Advection plus Diffusion:

Both advection and diffusion are usually active simultaneously and they are **linear processes**, therefore, their governing equations are additive yielding what's known as the advective diffusion equation.

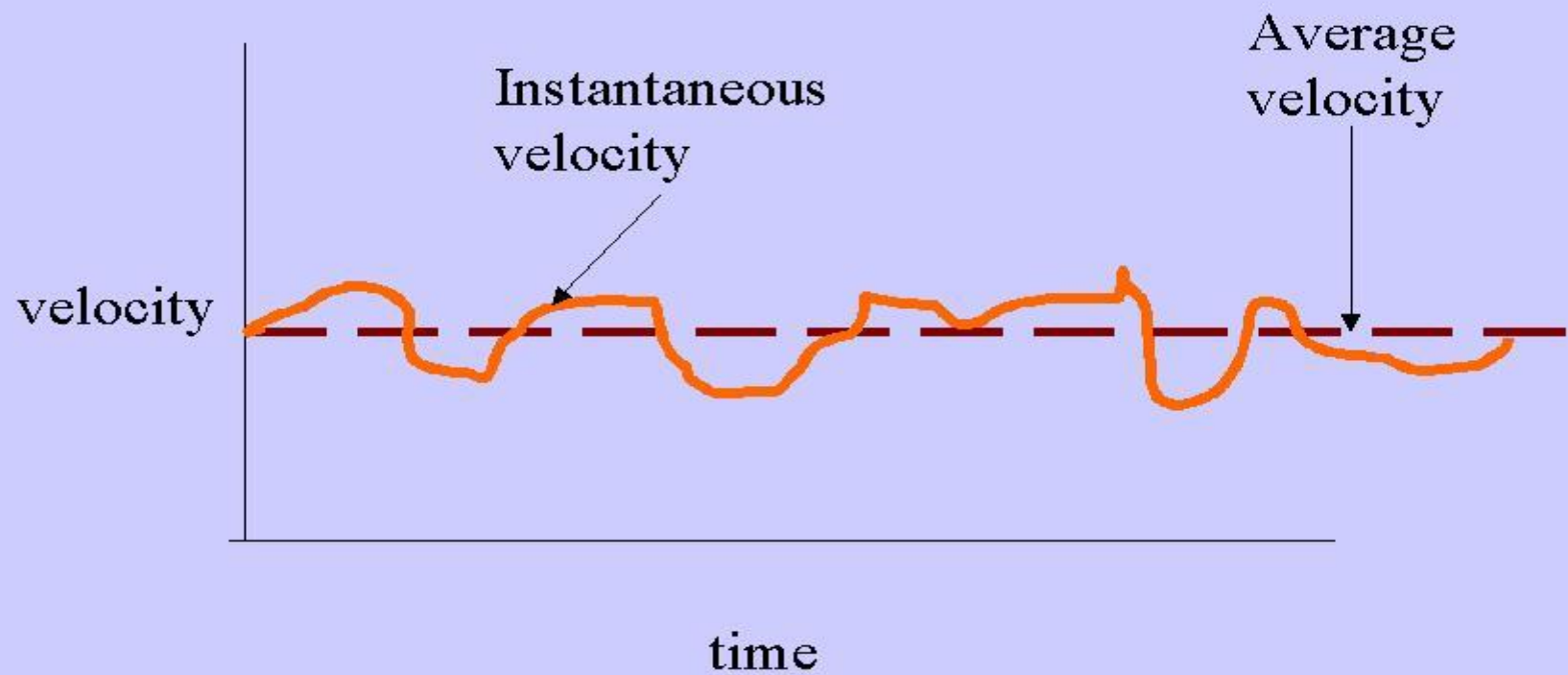
$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} + w \frac{\partial C}{\partial z} = D \frac{\partial^2 C}{\partial x^2} + D \frac{\partial^2 C}{\partial y^2} + D \frac{\partial^2 C}{\partial z^2}$$

Additionally there are two other diffusive type transport mechanisms active in most environmental engineering processes.

Turbulent Diffusion and Shear Flow Dispersion.

TURBULENT DIFFUSION

Basically turbulent diffusion is due to random fluctuation in advective velocity. A typical one dimensional velocity history at a single point in a turbulent velocity field might look like the figure below.



It's very difficult to mathematically describe instantaneous velocity since it has a **random component**. Instantaneous velocity (u) has two components:

$\bar{u}$ = avg. velocity

u' = perturbation velocity

u = instantaneous velocity

$$u = \bar{u} + u'$$

The effect of these velocity perturbations is increased mixing in the form of increased diffusion. We can model this increased diffusion as follows:

$$\frac{\partial C}{\partial t} + (\bar{u} + u') \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial x^2}$$

On the average there is no increase in the net advective velocity due to turbulent fluctuations so we model the effect in the diffusional term.

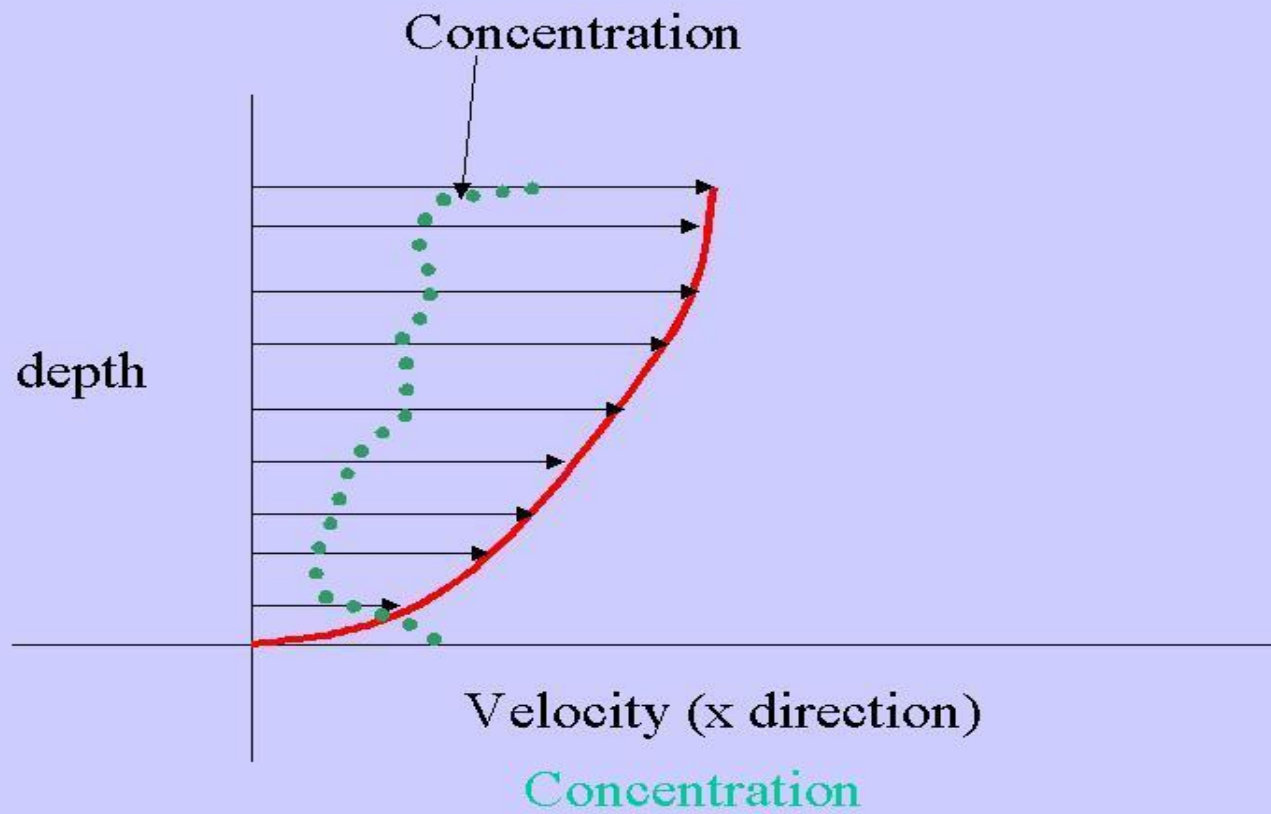
$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = (D + e) \frac{\partial^2 C}{\partial x^2}$$

Where “e” = turbulent diffusion coefficient.

SHEAR FLOW DISPERSION

If a velocity profile exists and if there is molecular or turbulent diffusion we get shear flow dispersion. Shear flow dispersion occurs even under laminar flow conditions. (laminar flow means no turbulence – flow streamlines are parallel). Shear flow dispersion is a result of the interaction of turbulent and molecular diffusion and shear velocity.

A typical velocity profile (in the x-direction) is shown below. The differential velocity at each depth, coupled with molecular diffusion and/or turbulent diffusion and a concentration profile (of the material being mixed) transverse to this velocity results in shear flow dispersion (mixing in the direction of flow).



Once again this type of diffusion is included in the diffusive term of the advective diffusion equation. So the resulting advective-diffusion equation finally looks like:

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = (D + e + E_L) \frac{\partial^2 C}{\partial x^2}$$

Where E_L is the longitudinal dispersion coefficient (i.e., dispersion in the direction of flow).

All types of diffusion and dispersion are often combined into an overall diffusion coefficient call D_d because it is difficult to separate the individual contributions of each.

Where $D_d = D + e + E_L$ In many reactors longitudinal dispersion dominates so D_d is approximated by E_L .

Determination of Reactor Characteristics

Mass transfer in reactors results from *advection* (bulk fluid transport) and *diffusion (mostly dispersion)*. Mixing level is quantified by the diffusion (dispersion) coefficient, D_d [cm^2/sec , or similar units]).

The relative importance of advective transport vs. dispersion is characterized by a dimensionless parameter called the Peclet Number (Pe), defined as:

$$Pe = \frac{L \cdot U}{D_d}$$

Where:

L = characteristic length (usually reactor length) [L];

U = advective velocity [L/T];

D_d = dispersion coefficient [L^2/T].

As discussed previously, mixing levels give rise to three categories of reactors.

- Plug-flow (PF) represents no axial dispersion,
 $Pe = \infty$
- Complete-mix flow (CMF) with infinite dispersion,
 $Pe = 0$.
- Flow with dispersion (FD), $0 < Pe < \infty$

One of the easiest methods to determine reactor mixing characteristics is to input a spike or instantaneous slug of conservative material at $t = 0$ and then monitor the reactor effluent response.

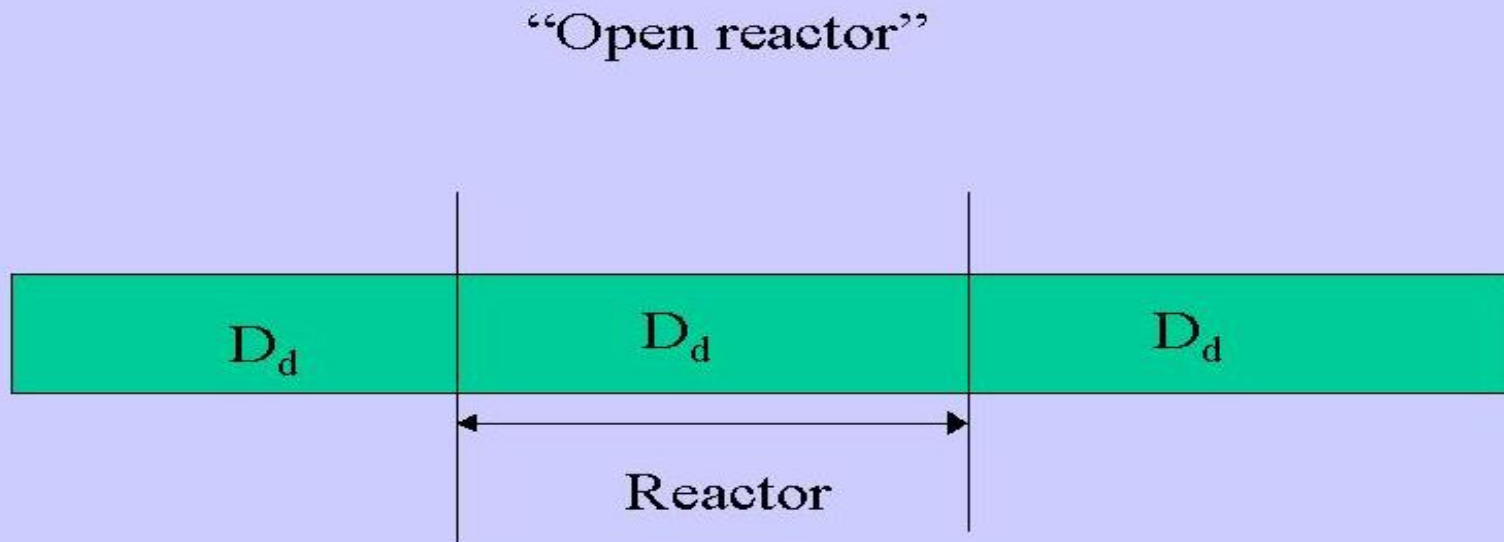
Start with the most realistic type of reactor - flow with dispersion (**FD**).

Analysis of this problem can begin by spiking the reactor with a mass M of conservative material at $t = 0$. First assume that there is no advection and that the only mixing mode is molecular diffusion in the x -direction. 1-D solution to the advective-diffusion equation with no advection and $D_d = D$. is given by:

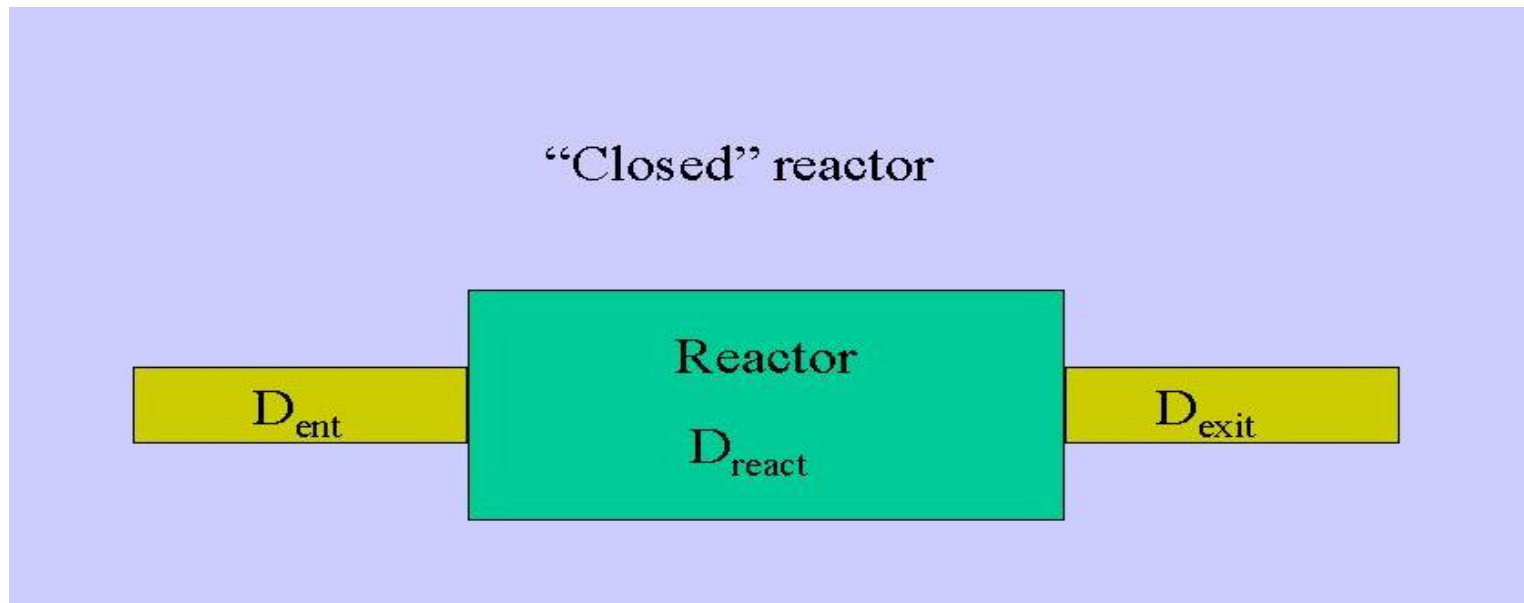
$$C(x, t) = \frac{M}{A\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

Note that this 1-D solution implies that there is uniform concentration "distribution" in the y-z plane (cross-sectional area A) and diffusional transport in the x (axial) direction only. In other words the initial mass M of conservative material is distributed uniformly over cross-sectional area (A) so that the "concentration" is actually mass/area. This implies that there is zero thickness to the input. Physically this is impossible but it is mathematically convenient and the approximation does not impact the solution greatly.

The boundary conditions used to find the above solution assumes that the diffusion coefficient at the exit and entrance to the reactor are the same as in the reactor. This is called an "open" reactor. This is equivalent to letting the reactor be defined as a section of a long reactor as shown here:



A "closed" reactor is one where the reactor has a diffusion or dispersion coefficient different than those of the entrance or exit. Typically exit and entrance diffusion/dispersion are much less than the diffusion/dispersion in the reactor. This system is shown schematically as:



There are no analytical solutions for a “closed” system. Numerical solutions are available for a variety of initial conditions. For our analysis we’ll work with open system analysis and correct when necessary for closed system conditions. So let’s continue with an open system analysis by adding advection to the process, i.e., let flow pass continuously through the reactor.

If we have advection we will most likely get shear dispersion and turbulent diffusion in addition to molecular diffusion. (i.e., use D_d instead of D).

Also we can transform distance (x) by moving with the avg. fluid flow by defining $x' = x - ut$ to get:

$$C(x', t) = \frac{M}{A\sqrt{4\pi D_d t}} \exp\left(-\frac{(x - u \cdot t)^2}{4D_d t}\right)$$
$$= \frac{M}{A\sqrt{4\pi D_d t}} \exp\left(-\frac{x'^2}{4D_d t}\right)$$

In a flowing system this is equivalent to injecting the conservative material in an infinitely thin plane at $t = 0$ and $x = 0$ (at the entrance of the reactor) so that the "concentration" at this point is M/A . By transforming distance (x) as we did above we are effectively riding with the initial spike of material so that we are only observing diffusion.

Note that x' is the *relative* distance-- in the x dimension-- from the position of peak concentration; the peak will always be located at $x = u t$. Negative values of x' thus represent positions upstream from the peak and positive values represent positions downstream from the peak.

If time (t) is fixed it turns out that the form of this equation for $C(x')$ is exactly the form of the normal frequency distribution (Gaussian) curve which has the general form:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{x^2}{2\sigma^2}\right)$$

If the $C(x')$ function is normalized by $(A \cdot M)^{-1}$ we can write:

$$C'_{x'} = \frac{1}{\sigma_{x'} \sqrt{2\pi}} \exp\left(-\frac{x'^2}{2\sigma_{x'}^2}\right)$$

$C'_{x'}$ = normalized, x' -dependent concentration
= $C_{x'}(A \cdot M)^{-1}$ (i.e., the mass of constituent per unit reactor length per mass of constituent initially pulse-discharged) $[L^{-1}]$.

$\sigma_{x'}^2$ = variance in x' (i.e., a measure of the Gaussian profile's spread in the x dimension-symmetrically on either side of the peak - at a fixed time) $[L^2]$.

By analogy to the $C(x',t)$ expression:

$$\sigma_x = \sqrt{2D_d t}$$

In other words if we measure the spread (standard deviation) of the response curve (of a spike input) we should be able to compute the dispersion coefficient for the reactor.

There are several ways to measure the response of a reactor to a spike input. The first is a synoptic measurement and the second is single point sampling.

Synoptic measurements. These measurements are taken from the perspective of “snapshots” of concentration vs. position (each snapshot at a different time), the pulse moves in the direction of advective flow (u), as a symmetrical Gaussian function, spreading ever wider with each successive snapshot. If we were to measure the variance with respect to x' in any fixed-time snapshot, we could estimate the applicable dispersion coefficient, D_d , via:

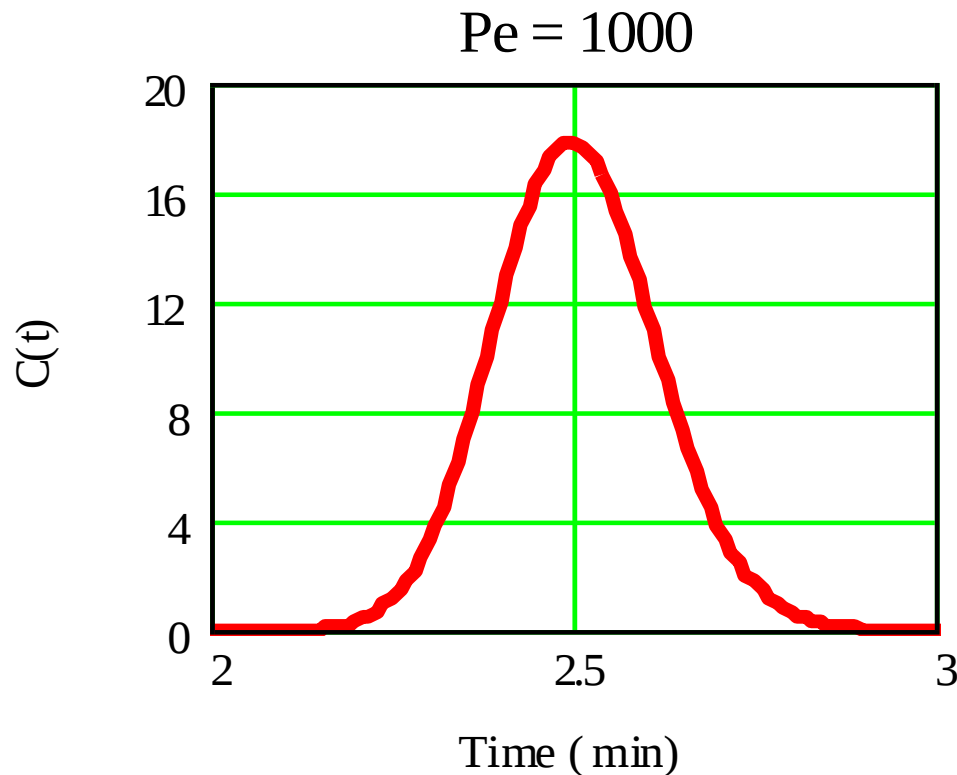
$$\sigma_x = \sqrt{2D_d t}$$

Such measurements taken at fixed times are called *synoptic*. In practice, they are difficult to make. They require coordination, as well as access to multiple sampling locations. The latter requirement is particularly difficult in many reactors.

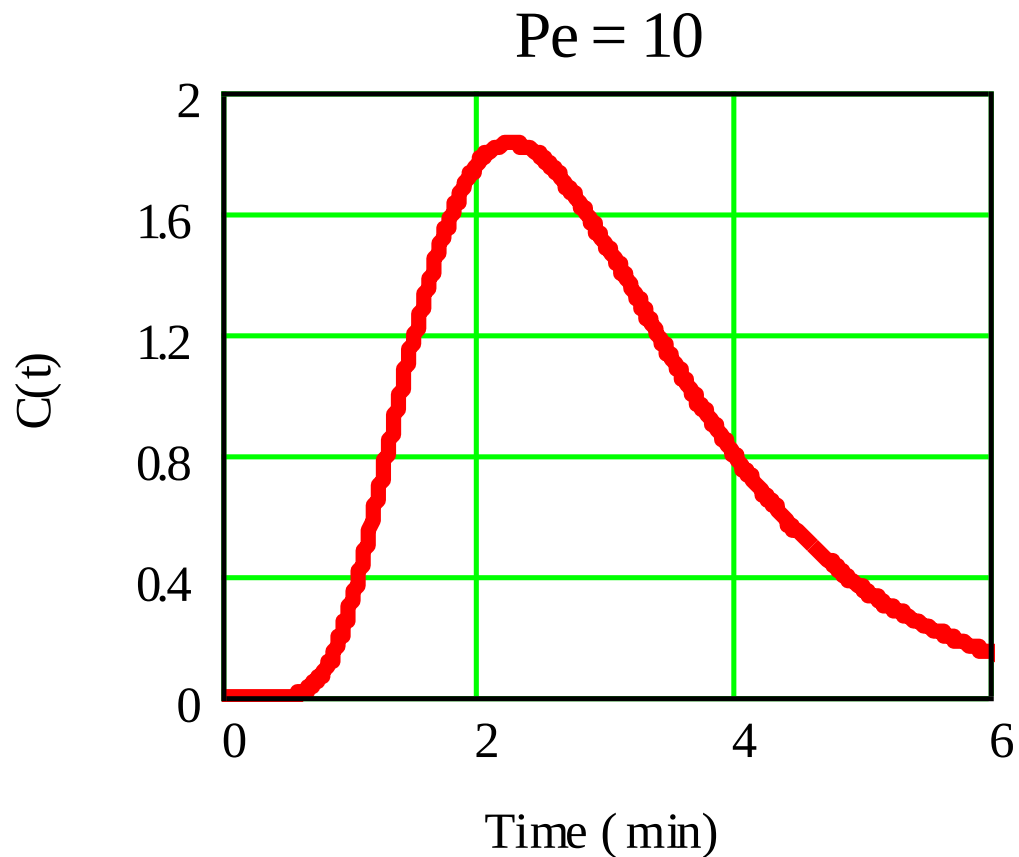
Single-point sampling. A more convenient option is to monitor the concentration vs. time at a fixed position along the x axis of the reactor — usually at the effluent end. Then x is no longer a variable and $C(x,t)$ becomes $C(t)$ only. In general, however, the resulting C vs. t data will not be symmetrical about the peak concentration value.

If dispersion is significant, our curve (which appears Gaussian if examined vs. x' at any constant time) will have “spread and slumped” significantly in the time it takes to pass the monitoring point. This makes the leading edge of the concentration profile appear steeper, sharper than the trailing edge.

For example look at the single point sampling results for two different diffusion coefficients. First, a relatively **low** diffusion coefficient (**high** Pe):



Then for a relatively **high** diffusion coefficient (**low** Pe):



If the dispersion coefficient is relatively small, the symmetry of the response curve is not upset at the sampling point. However, if we have high dispersion the curve "spread" changes dramatically during the sampling period and we get a skewed response curve. The variance in the data may still be defined as follows — in this case, it is σ_t^2 , the variance in time from the mean hydraulic retention time, $\bar{t}$.

$$\sigma_t^2 = \frac{\int_0^\infty C \cdot (t - \bar{t})^2 dt}{\int_0^\infty C dt} = \frac{\int_0^\infty t^2 \cdot C dt}{\int_0^\infty C dt} - \bar{t}^2$$

$$\bar{t} = \frac{\int_0^\infty t \cdot C dt}{\int_0^\infty C dt}$$

For discrete data points:

$$\sigma_t^2 \cong \frac{\sum_i t_i^2 \cdot C_i \Delta t_i}{\sum_i C_i \Delta t_i} - \bar{t}^2$$

$$\bar{t} \cong \frac{\sum_i t_i \cdot C_i \Delta t_i}{\sum_i C_i \Delta t_i}$$

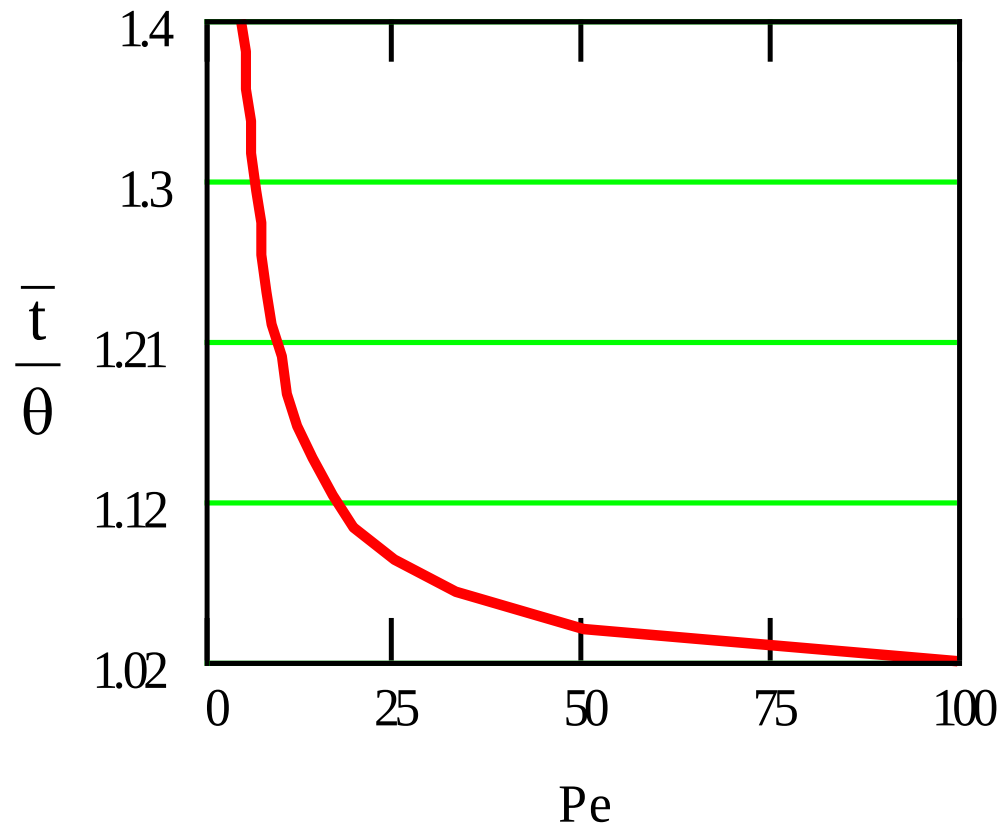
Detention Time Determination for Real Reactors:

Given the possible skewness of the C vs. t profile for single point sampling, the mean predicted retention time, $\bar{t}$, will, in general, be *greater than* the time at which the peak concentration passes the monitoring point, $\theta = V/Q$ (i.e., reactor volume divided by flowrate, or reactor length divided by advective velocity).

$\bar{t}$ is predicted by :

$$\bar{t} = \frac{\int_0^{\infty} t \cdot \frac{M}{A \sqrt{4\pi D_d t}} \exp\left(-\frac{(x-u \cdot t)^2}{4D_d t}\right) dt}{\int_0^{\infty} \frac{M}{A \sqrt{4\pi D_d t}} \exp\left(-\frac{(x-u \cdot t)^2}{4D_d t}\right) dt}$$

Integration of this expression is difficult but a numerical technique can be used to show the effect of Pe on the ratio of $\bar{t}$ to θ .



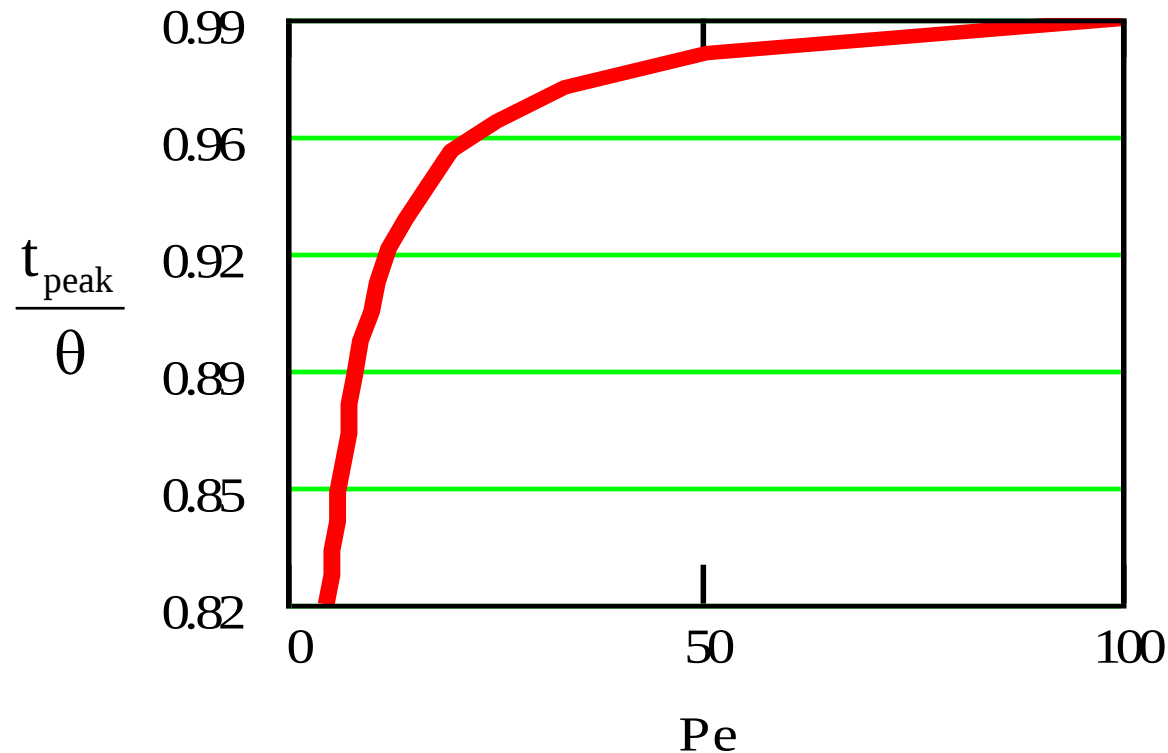
The reason for ratio values greater than unity is the nature of an open system. An open system will allow material to diffuse upstream from the reactor inlet boundary. This effectively increases the material residence time within the prescribed boundaries of the reactor.

To estimate the reactor residence time using time of peak tracer concentration at the effluent sampling site only works with low dispersion for open or closed systems. As dispersion increases an adjustment must be made.

For open systems the magnitude of this adjustment can be determined by differentiating the $C(t)$ expression with respect to t and setting the result equal to zero to find the time of maximum concentration, t_{peak} . The result of this is:

$$\frac{t_{\text{peak}}}{\theta} = \sqrt{\left(\frac{1}{\text{Pe}}\right)^2 + 1} - \frac{1}{\text{Pe}}$$

As Pe becomes large (low dispersion) the time to peak approaches θ . The plot below demonstrates this.



For closed systems there is still a shift in observed peak concentration time relative to θ as dispersion increases. However, since there is no analytical solution to the closed system problem we can't easily differentiate the response curve. Qualitatively the shift is greater than the open system shift. For example, for $Pe = 5$ the open system shift is 0.82 (the peak is observed at 0.82 of θ) while the closed system shift (calculated numerically) is 0.65 (the peak is observed at 0.65 of θ). For $Pe = 40$ the shifts are closer; 0.92 for the closed system and 0.975 for the open system.

Note that for synoptic sampling there is no skewness to the $C(t)$ curve and hence no corrections are needed. Since real reactors lie somewhere between "open" and "closed" estimation of true residence time can be difficult. The best estimation of true residence time comes from analysis of tracer data using.

$$\bar{t} \cong \frac{\sum t_i \cdot C_i \Delta t_i}{\sum_i C_i \Delta t_i}$$

This equation will give good estimates of "effective" residence time for both open and closed systems.

Estimation of D_d using variance of $C(t)$

In synoptic monitoring, $\sigma_x'^2$ can be used to estimate D_d in a rather direct manner, as earlier presented. In analogous fashion, σ_t^2 can be used, from single-point monitoring, to estimate D_d ; however, response curve skewness makes the symmetrical normal distribution curve inappropriate and a new relationship between the variance and the dispersion coefficient (or Pe) has to be determined. Boundary conditions (where and how the dye is injected and sampled) affect the dispersion (or at least the determination of it).

To determine σ_t^2 (variance for a single point sampling) use:

$$\sigma_t^2 = \frac{\int_0^\infty t^2 \cdot C dt}{\int_0^\infty C dt} - \bar{t}^2$$

with

$$C(x, t) = \frac{M}{A\sqrt{4\pi D_d t}} \exp\left(-\frac{(x-u \cdot t)^2}{4D_d t}\right)$$

and

$$\bar{t} = \frac{\int_0^\infty t \cdot C dt}{\int_0^\infty C dt}$$

Again the integration of $C(t)$ is difficult and requires a Gamma function to solve. The result of these computations is a relationship between Pe and σ_t^2 given by:

$$\sigma_t^2 = \theta^2 \cdot \left(\frac{2}{Pe} + \frac{8}{Pe^2} \right)$$

For a closed system the $C(t)$ response curve and the calculations are done numerically to give:

$$\sigma_t^2 = \theta^2 \cdot \left[\frac{2}{Pe} - \frac{2}{Pe^2} (1 - e^{-Pe}) \right]$$

Note that the units of σ_t are time.

The estimation of true θ is sometimes problematic because estimating the effective volume is difficult because of possible short-circuiting. One method to detect short-circuiting is to check that:

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

i.e., you should be able to account for all the mass added as a spike. If measured mass in the effluent is less than M added there is probably some short-circuiting.

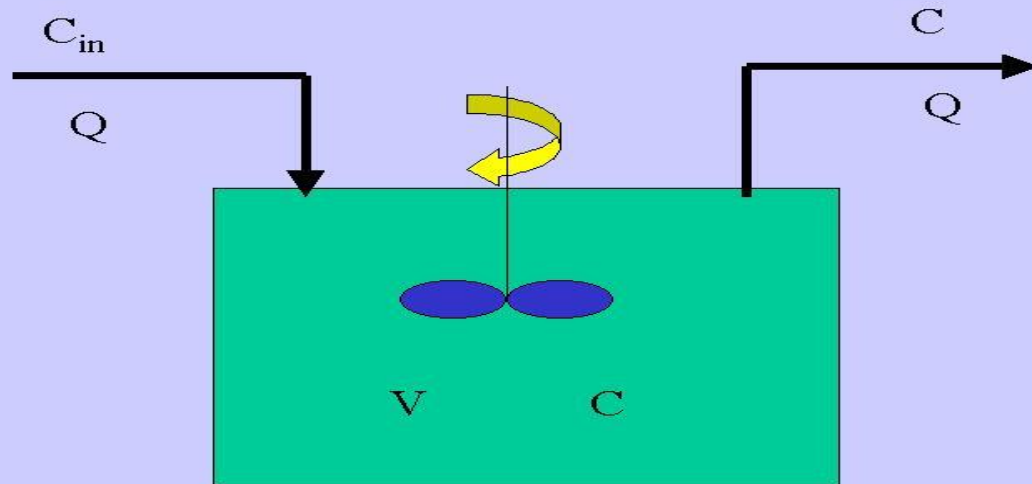
Most real reactors are of the arbitrary flow (i.e., FD), and the above analysis is appropriate. In some cases a reactor will approach the extremes in Pe where Pe approaches zero (CMF) or infinity (PF). In both these cases, analysis of the reactors is much easier than for a FD reactor. So, when possible, we try to approximate reactors by the CMF or PF type.

Plug Flow and Complete Mix Reactors

Using the advective diffusion equation to model and characterize transport in these reactors (which recall are only limiting cases) is difficult because D_d is either infinite or zero. Rather than try to solve the advection-diffusion equation for a variety of boundary conditions a more convenient (and easier) method is to perform mass balances about the reactor.

For the **CMF** reactor:

Perform a mass balance on a conservative substance:

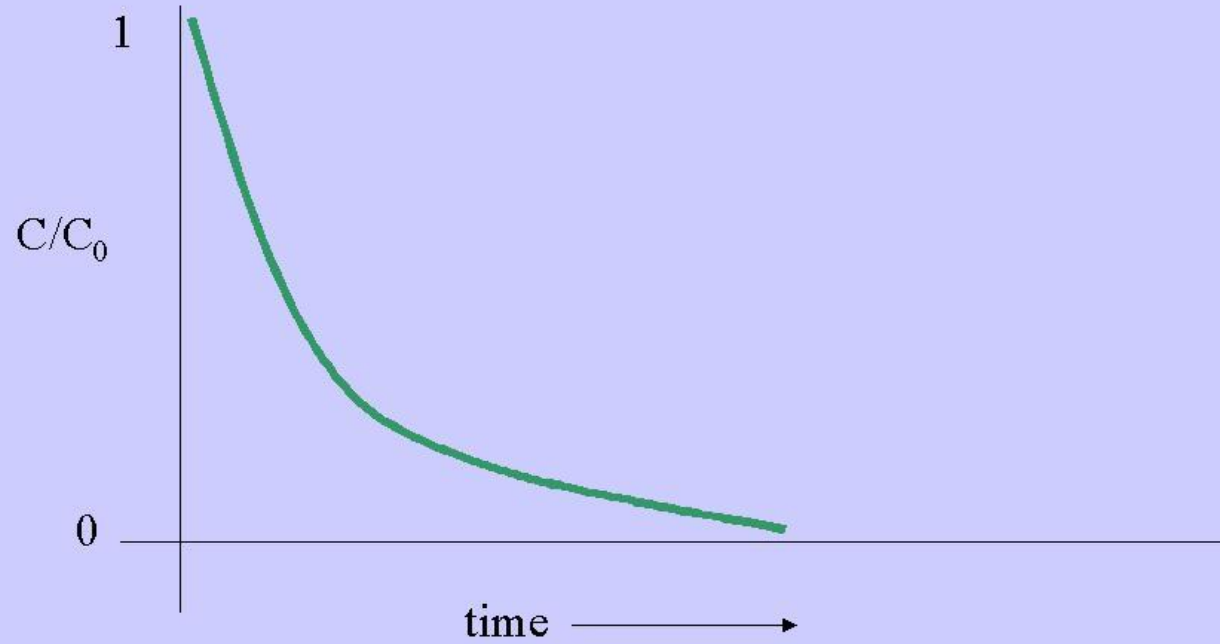


$$(C_{in} \cdot Q) - (C \cdot Q) = V \frac{dC}{dt}$$

$$\frac{C_{in}}{\theta} - \frac{C}{\theta} = \frac{dC}{dt}$$

This differential equation can be solved for a variety of system inputs. For example, consider an impulse (spike input) loading. A mass M is discharged instantly into the reactor at $t = 0$ so that the initial concentration in the reactor is $C_0 = M/V$. The solution to the differential equation with $C = C_0$ at $t = 0$ as initial conditions is:

$$C = C_0 \exp\left(-\frac{t}{\theta}\right)$$



Since:

$$\bar{t} = \int_0^{\infty} t \cdot C(t) dt / \int_0^{\infty} C(t) dt$$

where:

$$C(t) = C_0 \exp\left(-\frac{t}{\theta}\right)$$

We can easily show that:

$$\bar{t} = \frac{V}{Q}$$

i.e., the measured hydraulic residence time should equal the theoretical detention time.

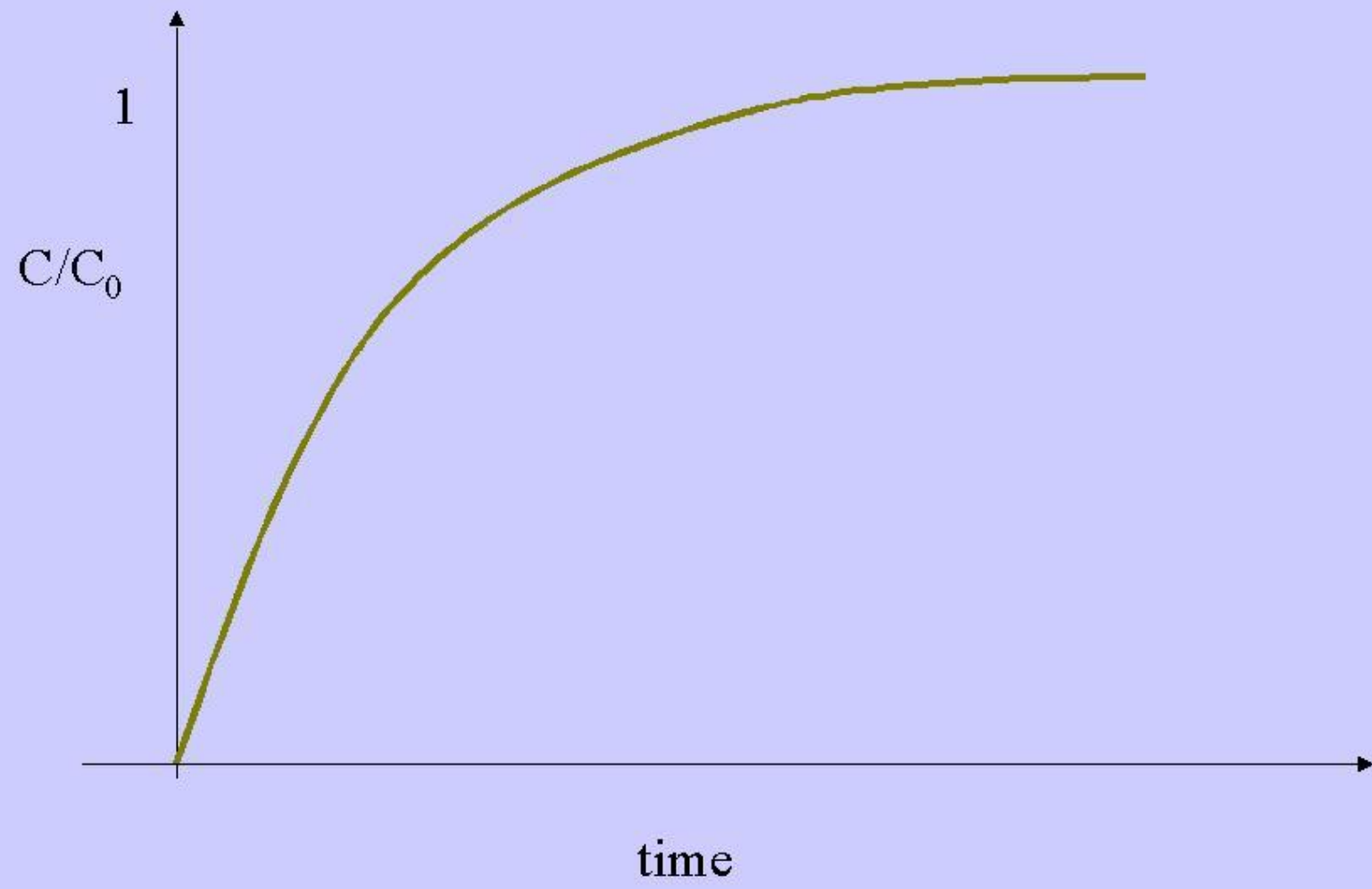
Another common initial condition, a *step input*, can be defined where:

$$C_{\text{in}} = 0 \quad \text{for } t < 0$$

$$C_{\text{in}} = C_0 \quad \text{for } t \geq 0$$

The solution to the governing differential equation for the CMF for this step input is given by:

$$C = C_0 \left(1 - \exp\left(-\frac{t}{\theta}\right) \right)$$

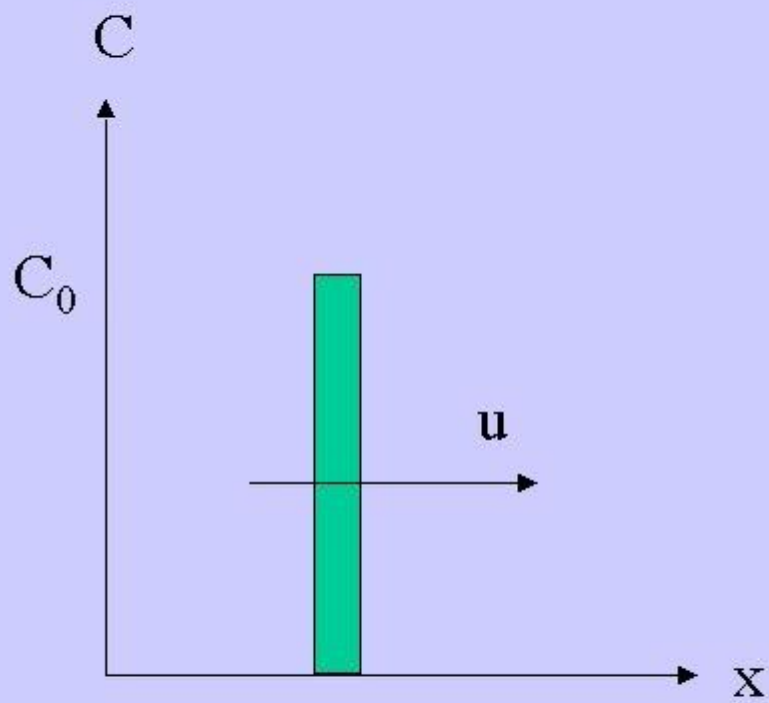


Plug Flow Reactors:

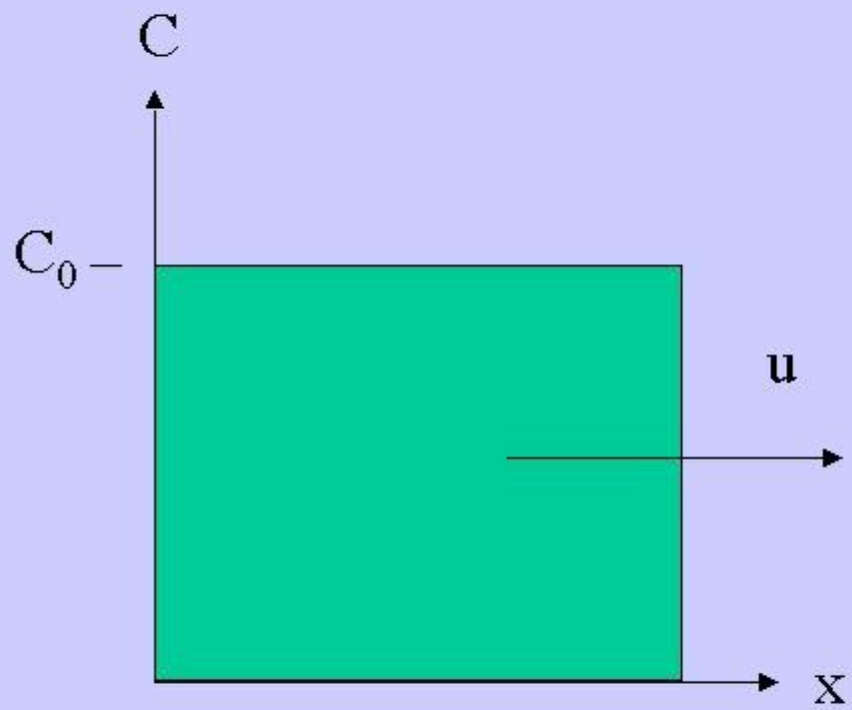
Plug Flow regimes are impossible to attain in practice because mass transport must be by advection alone. (There can be no differential displacement of material relative to the average advective velocity). This type of flow is often referred to as “piston-type flow”. In practice some mixing will always occur because molecular diffusion, turbulent diffusion and fluid shear always exist in flowing systems. For the case of a plug-flow reactor, the advective diffusion equation reduces to:

$$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial x}$$

The velocity, u , serves to relate the directional concentration gradient into a temporal concentration gradient. In other words, a conservative substance moves with the advective flow of the fluid. The solution to the differential equation for a pulse input and for a step input are shown graphically in the following figure.



Pulse input



Step input

Reactor Transport and Reactions.

Most of the situations that we encounter in process engineering involve reactions (biological, chemical or physical). In many cases the reaction rate is either first order or can be linearized as a first order reaction.

This means:

$$\left(\frac{\partial C}{\partial t} \right)_{\text{rxn}} = -kC$$

If the reaction term is linear it can be added to the advection-diffusion equation by the principle of superposition. The result is:

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = D_d \frac{\partial^2 C}{\partial x^2} + R$$

where R is a first order decay reaction.

Application to reactors

First consider the PDF reactor. The governing equation is again the advective-diffusion equation:

$$\frac{\partial C}{\partial t} = D_d \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - kC$$

The steady-state ($dC/dt = 0$) solution of this equation for a steady input of $C = C_0$ for $t > 0$ for reactor of length L is given by the Werner - Wilhelm equation:

$$\frac{C_{out}}{C_0} = \frac{4 \cdot a \cdot \exp\left(\frac{1}{2d}\right)}{(1+a)^2 \exp\left(\frac{a}{2d}\right) - (1-a)^2 \exp\left(\frac{-a}{2 \cdot d}\right)}$$

$$a = \sqrt{1 + 4 \cdot k \cdot t \cdot d}$$

($t = L/u = \theta$ for the the effluent end of the reactor.)

$$d = \frac{1}{Pe} = \frac{D_d}{L \cdot u}$$

CMF Reactors:

As before the advective diffusion equation is not very useful for CMF or PF reactors. For the case of **CMF** reactor the mass balance approach can be used. If we apply a first order reaction in a **CMF** reactor the governing equation (derived from a mass balance) is:

$$-V k C + Q \cdot C_{\text{in}} - Q \cdot C = V \frac{dC}{dt}$$

The solution to this differential equation for the initial condition that $C = C_{\text{initial}}$ at $t = 0$ in the tank and $C = C_0$ for the continuous inflow concentration (which is maintained for $t > 0$) is given by:

$$C = \frac{Q \cdot C_0}{V \left(k + \frac{1}{\theta} \right)} \left(1 - e^{-t \left(k + \frac{1}{\theta} \right)} \right) + C_{\text{init}} e^{-t \left(k + \frac{1}{\theta} \right)}$$

Most of our process design and analysis is for steady-state where there is no net accumulation (or depletion) of mass in the reactor. In other words:

$$\frac{dC}{dt} = 0$$

Therefore at steady-state:

$$Q(C_0 - C) - V \cdot k \cdot C = 0$$

or:

$$1 - \frac{C}{C_0} - \frac{\theta \cdot k \cdot C}{C_0}$$

or:

$$\frac{C}{C_0} = \frac{1}{1 + k \cdot \theta}$$

(this result can also be attained by allowing $t \rightarrow \infty$ in the non-steady-state equation shown above).

PF Reactor:

Since dispersion is zero in a plug flow reactor we can write:

$$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial x} - kC$$

The steady-state governing equation ($\frac{\partial C}{\partial t}=0$) is given by:

$$u \frac{\partial C}{\partial x} = -kC$$

or:

$$-\frac{u}{k} \frac{\partial C}{C} = \partial x$$

For a continuous flow input with concentration $C_{\text{in}} = C_0$ and $C = 0$ in the reactor for $t < 0$ (although this doesn't matter at steady-state) and for reactor length L and $C = C_{\text{out}}$ at $x = L$ we can write:

$$-\frac{u}{k} \int_{C_0}^{C_{\text{out}}} \frac{\partial C}{C} = \int_0^L \partial x$$

Integration yields:

$$\frac{u}{k} \ln \left\{ \frac{C_{\text{out}}}{C_0} \right\} = -L$$

$$\frac{C_{\text{out}}}{C_0} = \exp \left\{ \frac{-L \cdot k}{u} \right\} = \exp \{ -\theta \cdot k \}$$

In a similar manner C at any other point along the reactor axis can be found by:

$$\frac{C_x}{C_0} = \exp\left\{\frac{-x \cdot k}{u}\right\}$$

Note that this solution also works for a pulse input discharged at $x = 0, t = 0$ at $C = C_0$ because the pulse input is just a snapshot of a segment of the continuous input solution.

Note for a pulse input inflow is always continuous, but the concentration of material in the inflow is not. The input pulse moves with the flow of at velocity u .

Location of the pulse at any time is thus found by $x = (u)(t)$. At that time and location C_x is given by the above equation. At all other values for x in the reactor $C = 0$.