



Fundamentals of Chemical Reactor Theory

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Introduction

In our everyday life we operate chemical processes, but we generally do not think of them in such a scientific fashion. Examples are running the washing machine or fertilizing our lawn. In order to quantify the efficiency of dirt removal in the washer, or the soil distribution pattern of our fertilizer, we need to know which transformation the chemicals will experience inside a defined volume, and how fast the transformation will be.

Chemical kinetics and reactor engineering are the scientific foundation for the analysis of most environmental engineering processes, both occurring in nature and invented by men. The need to quantify and compare processes led scientists and engineers throughout last century to develop what is now referred as Chemical Reaction Engineering (CRE). Here are presented the basics of the theory and some examples will help understand why this is fundamental in environmental engineering. All keywords are presented in bold font.

Reaction Kinetics

Reaction Kinetics is the branch of chemistry that quantifies rates of reaction. We postulate that an **elementary chemical reaction**¹ is a chemical reaction whose rate corresponds to a stoichiometric equation. In symbols:



¹for our purpose we will limit our discussion to elementary reactions

and the **reaction rate** will be defined as:

$$-r = k \cdot (c_A)^\alpha \cdot (c_B)^\beta \text{ II} \quad [2]$$

where k is referred as the specific reaction rate (constant). The overall **order of reaction** III is defined as:

$$n = \alpha + \beta. \quad [3]$$

The temperature dependency of k is described by the Arrhenius equation:

$$k(T) = A \cdot e^{-E_a/R \cdot T} \quad [4]$$

where, A = preexponential or frequency factor

E_a = activation energy [J/mol, cal/mol]

R = gas constant = 8.314 J/mol·K = 1.987 cal/mol·K

T = absolute temperature [K]

The Mass Balance

Mass is a conservative entity^{IV}, hence given a control volume V the sum of mass flows entering the system will equal the sum exiting minus (plus) the consumed (generated) or accumulated fractions:

$$\left\{ \begin{array}{c} \text{rate of} \\ \text{mass} \\ \text{in} \end{array} \right\} - \left\{ \begin{array}{c} \text{rate of} \\ \text{mass} \\ \text{out} \end{array} \right\} + \left\{ \begin{array}{c} \text{rate of} \\ \text{mass} \\ \text{generated} \end{array} \right\} - \left\{ \begin{array}{c} \text{rate of} \\ \text{mass} \\ \text{consumed} \end{array} \right\} = \left\{ \begin{array}{c} \text{rate of} \\ \text{mass} \\ \text{accumulated} \end{array} \right\} \quad [5]$$

shortly:

$$\boxed{\text{IN} - \text{OUT} + \text{PROD} - \text{CONS} = \text{ACC}} \quad [6]$$

Equation [6] represents the key point in **mass transfer**: analogously to the force balance in statics, the mass balance allows us to quantify and verify mass flows in our system.

Let us now apply this fundamental balance to some ideal examples.

Ideal Chemical Reactors

A **batch reactor**, as its name states, is a non-continuous and perfectly mixed closed vessel where a reaction takes place. Figure 1 shows a schematic drawing of it.

^{II} this is the reaction rate with respect to the reactants, the one with respect to the products being $-r = +k' \cdot (c_D)^\delta \cdot (c_E)^\epsilon$

^{III} rigorously, α is the order of reaction with respect to reactant A, and β with respect to B

^{IV} physicists would correct this statement, since energy is the only conservative entity; in all engineering applications, mass will be by far slower than light speed...



Fig. 1. Batch reactor

Given its volume V , and the initial internal concentration c_0 , the total mass will be $M = V \cdot c_0$. In the unit time, the concentration will be able to change only in virtue of a chemical reaction. The mass balance [6] quantifies this change: $IN - OUT + PROD - CONS = ACC$. In this case:

$$Q \cdot c_{in} - Q \cdot c_{out} \pm \int_V r dV = \frac{dm}{dt} \quad [7]$$

where r is the rate of generation (+) or depletion (-). Since the assumption of no flow in or out of the reactor volume ($Q = 0$), and constant reactor volume V ,

$$\frac{dm}{dt} = \frac{d(c \cdot V)}{dt} = V \cdot \frac{dc}{dt} = V \cdot r \quad [8]$$

where $c = c(t)$ is the concentration at any time inside the reactor^v. Then,

$$\frac{dc}{dt} = r. \quad [9]$$

The differential equation [9] is the **characteristic equation** of a batch reactor. Considering a **first-order reaction** ($r = -k \cdot c$):

$$\frac{dc}{dt} = -k \cdot c \quad [10]$$

solving,

$$\ln \frac{c}{c_0} = -k \cdot t \quad [11]$$

or

$$c = c_0 \cdot e^{-k \cdot t}. \quad [12]$$

Equation [12] offers a relationship between concentration and time. At any point in time, then, we can know the inner concentration, known the reaction constant and the initial concentration.

For a **second-order reaction** ($r = -k \cdot c^2$),

$$c = \frac{c_0}{1 + k \cdot c_0 \cdot t}. \quad [13]$$

^v Nota Bene: $c \neq c_{in}$!

This procedure may be repeated for any order of reaction, just substituting the expression for r in the characteristic equation [9]. N.B.: The algebraic passages will heretofore be omitted.

A **Continuous-Stirred Tank Reactor (CSTR)** is a well-mixed vessel that operates at steady-state ($Q_{in}=Q_{out}=Q$). The main assumption in this case is that the concentration of the incoming fluid will become **instantaneously** equal to the outgoing upon entering the vessel. Fig. 2 explains visually this concept.

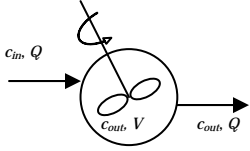


Fig. 2. Continuous-Stirred Tank Reactor

A CSTR differs from a batch only in the fact that it is not closed. Thus, the mass flows in and out of the reactor in eq. [6] will not cancel:

$$\frac{dm}{dt} = Q \cdot (c_{in} - c_{out}) + \int_V r \cdot dV = 0. \quad [14]$$

The mass balance in [14] equals to 0 thanks to the **steady state hypothesis** (=no accumulation). Solving,

$$c_{in} - c_{out} + \theta_H \cdot r = 0 \quad [15]$$

where $\theta_H = V/Q =$ average **hydraulic residence time**. Eq. [15] represents the characteristic equation for a CSTR. Assuming a **first-order reaction**,

$$\frac{c_{out}}{c_{in}} = \frac{1}{1 + k \cdot \theta_H}. \quad [16]$$

A **Plug Flow Reactor (PFR)** consists in a long, straight pipe in which the reactive fluid transits at steady-state (no accumulation). The main assumptions of this model are that the fluid is completely mixed in any cross-section at any point, but it experiences **no axial mixing**, i.e. contiguous cross-sections cannot exchange mass with each other. Fig. 3 illustrates it.



Fig. 3. Plug Flow Reactor

Operating a mass balance on the selected volume $\Delta V = A \cdot \Delta l$, and assuming steady-state conditions, we obtain

$$\frac{dm}{dt} = Q \cdot c_t - Q \cdot c_{t+\Delta t} + \int_{\Delta V} r \cdot dV = 0 \quad [17]$$

hence,

$$Q \cdot c_t - Q \cdot c_{t+\Delta t} + r \cdot \Delta V = Q \cdot c_t - Q \cdot c_{t+\Delta t} + r \cdot Q \cdot \Delta t = 0 \quad [18]$$

which reduces to

$$c_t - c_{t+\Delta t} + r \cdot \Delta t = 0 \quad [19]$$

or

$$\frac{\Delta c}{\Delta t} = r \quad [20]$$

Considering an infinitesimally thin cross-sectional volume, its thickness will reduce to dl , therefore:

$$\frac{dc}{dt} = r \quad [21]$$

which, again, is the characteristic equation of the plug flow reactor. Considering a **first-order reaction**, the concentration equation will be

$$c = c_0 \cdot e^{-k \cdot t} \quad [22]$$

Segregated Flow Analysis

The non-ideality of industrial and natural processes lead engineers to develop corrections to the ideal models, in order to use them with less restrictions. For this reason, it is defined a **residence time distribution**, which is a function that describes the evolution of the average instantaneous concentration versus the elapsed time. It is very convenient to express the residence time distribution as the normalized function **E**,

$$E(t) = \frac{c(t)}{\int_0^{\infty} c(t) \cdot dt} \quad [23]$$

which has its total area under the curve equal to unity:

$$\int_0^{\infty} E(t) \cdot dt = 1 \quad [24]$$

Fig. 4 shows the evolution of **E** vs. time. The **E** curve is the distribution needed to account for non-ideal flow.

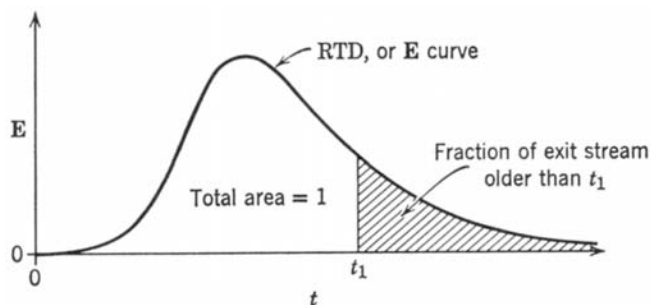


Fig. 4. The residence time distribution

Considering the definition of **E**, the average residence time will become:

$$\theta_H = \int_0^{\infty} t \cdot E(t) \cdot dt \quad [25]$$

An useful tool used in this field is the **cumulative residence time** fraction (or cumulative frequency) curve **F**, defined as:

$$F(t) = \int_0^{\infty} E(t) \cdot dt = \frac{\int_0^{t_i} c(t) \cdot dt}{\int_0^{\infty} c(t) \cdot dt} . \quad [26]$$

Equation 26 shows that the **F** curve at $t=t_i$ is defined as the cumulative area under the **E** curve from zero to t_i . This means that **F** represents the fraction of flow with a residence time $\leq t_i$. Combining [25] and [26]:

$$\theta_H = \int_0^1 t \cdot dF \quad [27]$$

which is the highlighted area in fig. 5. Note that the boundaries of the integral in [27] must be 0 to 1, since the area under the **E** curve equals unity.

Fig. 5. The cumulative frequency curve

The reason why we introduce the use of these functions is to quantify the non-ideality of reactors. A classic example is the evaluation of the average residence time. According to the ideal reactor theory, $\theta_H = V/Q$, where V is the total volume of the reactor. In case dead zones are present in the vessel, the residence time distribution will not account for them, showing a decreased reactor volume. Hence, θ_H calculated in both ways will give an estimate of the dead zone volume.

Fig. 6 illustrates the characteristic curves for various flows.

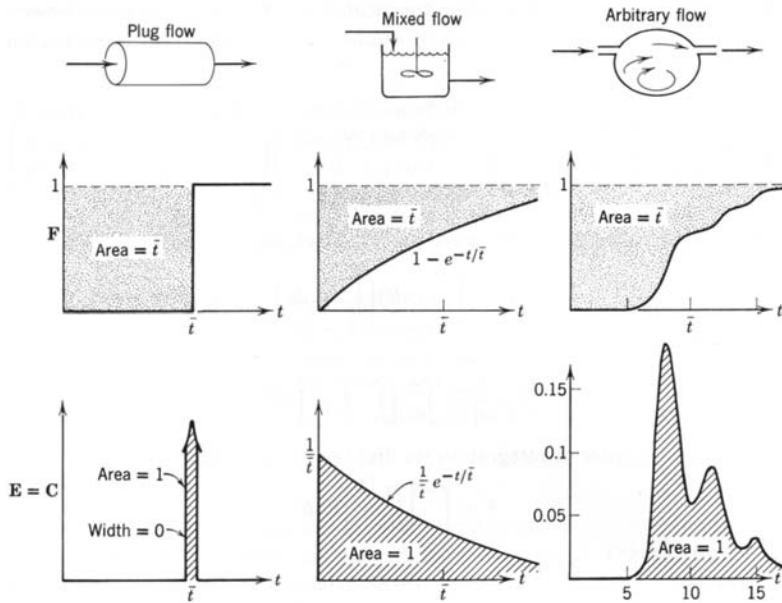


Fig. 6. Characteristic curves for various flows

Principles of Chemical Reaction Engineering

The effort to quantify **non-ideal** departures in chemical reactors leads to treat two main non-ideal models, the dispersion model, and the CSTR in series model. It belongs to common sense that if we inject a colored tracer into a flowing reactor, some of the dye will exit before the expected time (shot-circuiting), while some other will reside longer in the reactor (backmixing). In the case of a plug flow, the **dispersion model** accounts for axial dispersion D , which is the physical parameter that quantifies axial backmixing and short-circuiting of fluid. In a differential volume of flowing fluid:

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2} \quad [28]$$

analogous to Fick's first law on diffusion. Considering the whole flowing fluid, [28] will be corrected for the fluid motion through the introduction of an **advection** term:

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2} - u \cdot \frac{\partial c}{\partial x} \quad [29]$$

which, in its dimensionless form becomes

$$\frac{\partial c}{\partial t} = \left(\frac{D}{u \cdot L} \right) \cdot \frac{\partial^2 c}{\partial z^2} - \frac{\partial c}{\partial z} \quad [30]$$

where, L = reactor length

u = fluid velocity in the reactor

D = dispersion coefficient [cm^2/s]

and the dimensionless group $\left(\frac{u \cdot L}{D}\right)$ is called **Peclet number**, the parameter that quantifies the extent of axial dispersion, with limits:

$$\left(\frac{u \cdot L}{D}\right) \rightarrow 0 \quad \text{negligible dispersion (plug flow)}$$

$$\left(\frac{u \cdot L}{D}\right) \rightarrow \infty \quad \text{large dispersion (mixed flow).}$$

Fig. 7 shows concentration curves in closed vessels for various extents of backmixing quantified through the dispersion model.

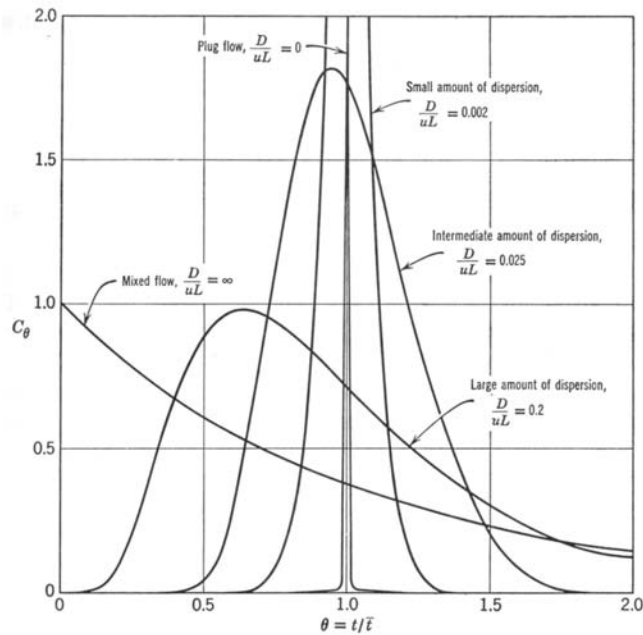


Fig. 7. Concentration curves at different Peclet numbers

The **CSTR-in-series model** considers a sequence of completely mixed tanks as a fit to sequential zones of the non-ideal reactor. In a sense, this is similar to considering the PFR as a sequence of non-interacting differential volumes. Thus, both the **E** and **F** curves will be the sum of a series:

$$E_N = \frac{N}{\theta} \cdot \left(\frac{N \cdot t}{\theta}\right)^{(N-1)} \cdot \frac{e^{-N \cdot t/\theta}}{(N-1)!} \quad [31]$$

and

$$F_N = 1 - \left\{ e^{-N \cdot t/\theta} \cdot \sum_{i=1}^N \left[\frac{1}{(i+1)!} \cdot \left(\frac{N \cdot t}{\theta}\right)^{(i-1)} \right] \right\} \quad [32]$$

Fig. 8 visualizes this concept for the **F** curve.

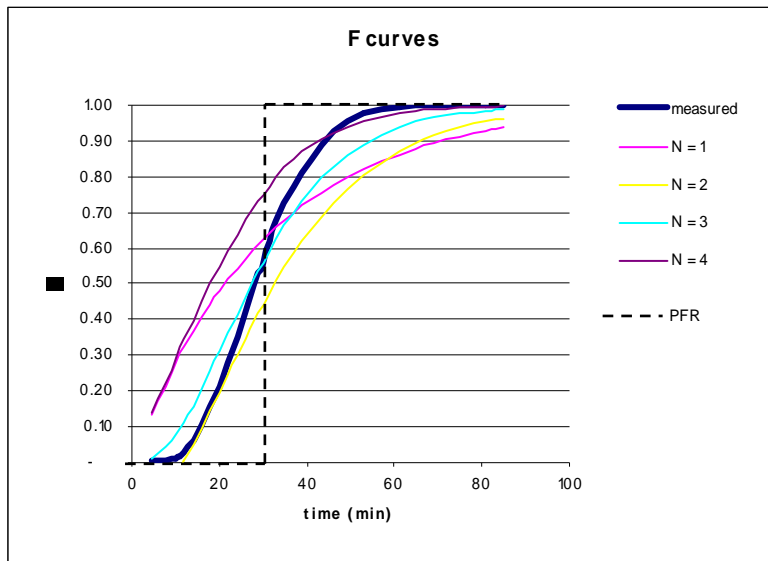


Fig. 8. Cumulative concentration curves for different numbers of CSTR in series. N= number of reactor. A PFR diagram is dashed.

Bibliography

The books here quoted have to be used for reference only, as they are too advanced for the purpose of this class. We strongly recommend keeping the list as a reference for possible future need, as the books quoted represent the most important works in chemical engineering today.

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