FUNDAMENTALS OF CHEMICAL REACTOR THEORY

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Abstract. In our everyday life we operate chemical processes, but we generally do not think of them in 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 natural and human made. 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 used herein are presented in *italic* font.

Contents

1. Reaction Kinetics

Reaction kinetics is the branch of chemistry that quantifies rates of reaction. Even though this branch treats all types of chemical reactions, herein, however, we limit the treatment to *elementary chemical reactions*. An elementary reaction is a chemical reaction whose rate corresponds to a stoichiometric equation.

Consider, for instance, a chemical process where k reactants $\{\mathrm{R}_i \,|\, i : 1 \to k\}$ yield l products $\{\mathrm{P}_j \,|\, j : 1 \to l\}$; *i.e.*,

$$\sum_{i=1}^{k} \nu_i \mathrm{R}_i \longrightarrow \sum_{j=1}^{l} \nu_j \mathrm{P}_j \,.$$

Then, define the *reaction rate*, r, by

$$-r = \prod_{i=1}^{k} c_{\mathrm{Ri}}^{\nu_i} \,,$$

where c_{Ri} is the concentration of the i-th reactant, and define the overall *order of reaction*, n, by

$$n = \sum_{i=1}^{k} \nu_i \,.$$

Note that, if $\dim c_{\mathrm{R}} = [\mathsf{N}/\mathsf{L}^3]$, then $\dim r = [\mathsf{N}/\mathsf{L}^3\mathsf{T}]$ and $\dim n = [1]$.

The reaction rate depends on many factors:

- The nature of the reaction: some reactions are naturally faster than others. The number of reacting species, their physical state (the particles that form solids move much more slowly than those of gases or those in solution), the complexity of the reaction and other factors can greatly influence the rate of a reaction.

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- Concentration: reaction rate increases with concentration, as described by the rate law and explained by collision theory. As reactant concentration increases, the frequency of collision increases.
- Pressure: the rate of gaseous reactions increases with pressure, which is, in fact, equivalent to an increase in concentration of the gas.The reaction rate increases in the direction where there are fewer moles of gas and decreases in the reverse direction. For condensed-phase reactions, the pressure dependence is weak.
- Order: the order of the reaction controls how the reactant concentration (or pressure) affects reaction rate.
- Temperature: usually conducting a reaction at a higher temperature delivers more energy into the system and increases the reaction rate by causing more collisions between particles, as explained by collision theory. However, the main reason that temperature increases the rate of reaction is that more of the colliding particles will have the necessary activation energy resulting in more successful collisions (when bonds are formed between reactants). The influence of temperature is described by the Arrhenius equation, explained below. As a rule of thumb, reaction rates for many reactions double for every 10 degrees Celsius increase in temperature, though the effect of temperature may be very much larger or smaller than this.

Example. Consider a chemical reaction of a moles of A and b moles of B that yield c moles of C and d moles of D or, symbolically,

$$\mathrm{aA} + \mathrm{bB} \longrightarrow \mathrm{cC} + \mathrm{dD}\,.$$

Calculate the reaction rate and the order of reaction.

Solution. By definition, the reaction rate is $-r = \kappa c_{\mathrm{A}}^{a} c_{\mathrm{B}}^{b}$ and the order of reaction $n = a + b$.

The dimensions of the rate coefficient depend on $\dim n$ and on $\dim c$. If concentration has dimensions of $[\mathsf{N}/\mathsf{L}^3]$, then, for an order n reaction, the rate coefficient has dimensions of

$$\mathsf{N}^{1-n}\mathsf{L}^{3(n-1)}/\mathsf{T}\,.$$

Example. Give the dimensions of the rate coefficient for an order zero reaction and an order one reaction.

Solution. For an order zero reaction, $n = 0$, the rate coefficient has dimensions of $[\mathsf{N}/\mathsf{L}^3\mathsf{T}]$ and, for an order one reaction, the rate coefficient has units of $[1/\mathsf{T}]$.

On the other hand, the rate coefficient depends on temperature. Such a dependency is described by Arrhenius equation:

$$\kappa[\theta] = A \exp[-e_{\mathrm{act}}/r_{\mathrm{gas}}\theta]\ ,$$

where A is the preexponential factor, e_{act} the activation energy, $[\mathsf{E}/\mathsf{N}]$, r_{gas} the gas constant, $[\mathsf{E}/\mathsf{N}\Theta]$, $8.314\,462\,1(75)$ J/mol K, and θ the thermodynamic (absolute) temperature, $[\Theta]$.

Alternatively, Arrhenius equation can be written as

$$\kappa[\theta] = A \exp[-e_{\mathrm{act}}/k_{\mathrm{bol}}\theta]\ ,$$

where k_{bol} is Boltzmann constant, $[\mathsf{E}/\Theta]$, $1.380\,648\,8(13) \times 10^{-23}$ J/K.

The difference between the two equations is the dimensions of e_{act}, because of the usage of either r_{gas} or k_{bol}: in the former, mostly used in chemistry, $\dim e_{\mathrm{act}}$ are energy per unit chemical amount; in the latter, mostly used in physics, $\dim e_{\mathrm{act}}$ are energy per molecule.

The dimensions of A are the same as the dimensions of κ; *i.e.*, $\dim A$ depends on the order of the reaction.

2. Mass balance

Mass is a conservative quantity, 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

FIGURE 1. Schema of a batch reactor

accumulated fractions:

$$\begin{pmatrix}\text{rate of mass}\\ \text{in}\end{pmatrix} + \begin{pmatrix}\text{rate of mass}\\ \text{out}\end{pmatrix} + \begin{pmatrix}\text{rate of mass}\\ \text{produced}\end{pmatrix} - \begin{pmatrix}\text{rate of mass}\\ \text{consumed}\end{pmatrix} = \begin{pmatrix}\text{rate of mass}\\ \text{accumulated}\end{pmatrix} .$$

The last statement 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.

2.1. **Ideal chemical reactors.**

2.1.1. *Batch reactors.* A *batch reactor* is a non-continuous, perfectly mixed and closed vessel where a reaction takes place, see fig. 1.

Given its volume v and the initial internal concentration of a species A, c_{A_0}, the total mass will be $m = vc_{\mathrm{A}_0}$. In the unit time, the concentration will be able to change only in virtue of a chemical reaction. The mass balance quantifies this change, in this case:

$$\phi_v c_{\mathrm{Ain}} - \phi_v c_{\mathrm{Aout}} \pm \int_v r \mathrm{d}v = \mathrm{d}_t m \,,$$

where r is the rate of generation (+) or depletion (−). Since the assumptions of no flow in or out of the reactor volume, $\phi_v = 0$, and constant reactor volume v,

$$\mathrm{d}_t m = \mathrm{d}_t c_{\mathrm{A}} v = v \mathrm{d}_t c_{\mathrm{A}} = vr \,,$$

where $c_{\mathrm{A}} = c_{\mathrm{A}}[t]$ is the concentration of A at any time t inside the reactor. Then,

$$\mathrm{d}_t c_{\mathrm{A}} = r \,,$$

The last differential equation is the *characteristic equation of a batch reactor*. Considering a *first-order reaction* ($r = -\kappa c_{\mathrm{A}}$), then

$$\mathrm{d}_t c_{\mathrm{A}} = -\kappa c_{\mathrm{A}} \,,$$

whose solution is

$$\frac{c_{\mathrm{A}}}{c_{\mathrm{A}_0}} = \exp[-\kappa t] \,,$$

or, in alternative forms,

$$\begin{aligned} \Gamma_{c_{\mathrm{A}}} &= \exp[-\Gamma_t] && \text{[dimensionless form]} \\ \overline{c_{\mathrm{A}}} &= \exp\left[-\bar{t}\right] \,. && \text{[scaled quantities form]} \end{aligned}$$

The last equations offer ways to relate concentration and time. At any t, we can know the concentration of A in the reactor, given the reaction constant and the initial concentration.

For a *second-order reaction* [1] ($r = -\kappa c_{\mathrm{A}}^2$),

$$\frac{c_{\mathrm{A}}}{c_{\mathrm{A}_0}} = \frac{1}{1 + \kappa c_{\mathrm{A}_0} t} \,.$$

[1] The algebraic passages will hereafter be omitted.

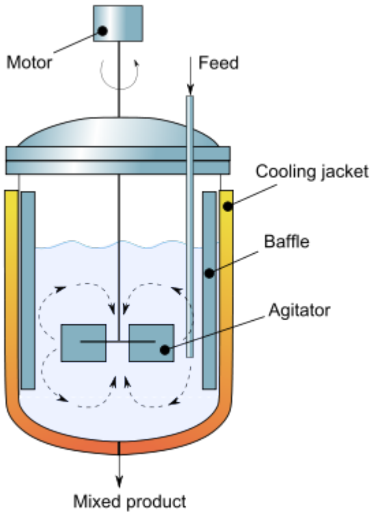

FIGURE 2. Schema of a continuous-stirred tank reactor

This procedure may be repeated for any order of reaction by substituting the expression for r in the characteristic equation.

2.1.2. *Continuous-stirred tank reactor.* A *continuous-stirred tank reactor*, CSTR, is a well-mixed vessel that operates at *steady-state*; *i.e.*, no mass accumulation in the reactor. The main assumption is that the concentration of the incoming fluid will become *instantaneously* equal to the outgoing upon entering the vessel, see fig. 2.

A CSTR differs from a batch only in the fact that it is not closed. Thus, the mass flowing in and flowing out of the reactor, terms in the mass balance, will not cancel:

$$\mathrm{d}_t m = \phi_v \left(c_{\mathrm{Ain}} - c_{\mathrm{Aout}}\right) + \int_v r \mathrm{d}v = 0\,.$$

Note, however, that the volumetric inflow and outflow are equal $\phi_{v_{\mathrm{in}}} = \phi_{v_{\mathrm{out}}} = \phi_v$ and that the term that does cancel is the accumulation, due to the steady state hypothesis. Solving the differential equation, one finds that

$$c_{\mathrm{Ain}} - c_{\mathrm{Aout}} + \tau_{\mathrm{h}} r = 0\,,$$

where $\tau_{\mathrm{h}} = v/\phi_v$ is the average *hydraulic residence time*. The last equation represents the *characteristic equation for a CSTR*. Assuming a *first-order reaction*, the model then becomes

$$\frac{c_{\mathrm{Aout}}}{c_{\mathrm{Ain}}} = \frac{1}{1+\tau_{\mathrm{h}}}\,.$$

2.1.3. *Plug flow reactor.* 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, see fig. 3.

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

$$\mathrm{d}_t m = \phi_v c_{\mathrm{A}}[t] - \phi_v c_{\mathrm{A}}[t+\Delta t] + \int_{\Delta v} r\,\mathrm{d}v = 0\,,$$

hence,

$$\phi_v c_{\mathrm{A}}[t] - \phi_v c_{\mathrm{A}}[t+\Delta t] + r\Delta v = \phi_v c_{\mathrm{A}}[t] - \phi_v c_{\mathrm{A}}[t+\Delta t] + r\phi_v\Delta t = 0 \implies \frac{\Delta c_{\mathrm{A}}}{\Delta t} = r\,.$$

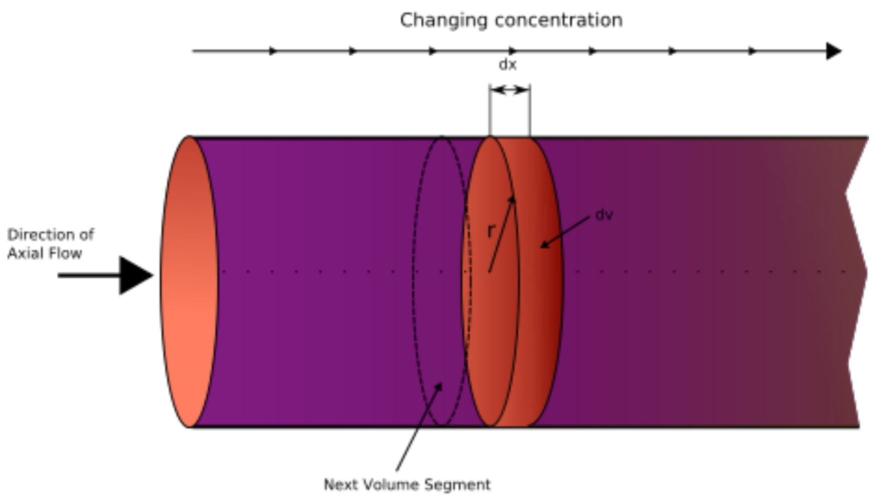

FIGURE 3. Schema of a plug flow reactor

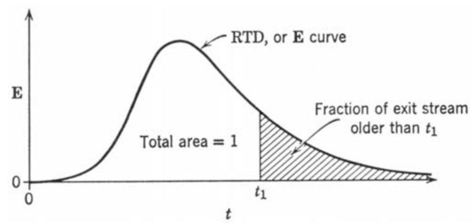

FIGURE 4. Residence time distribution: exit age distribution curve

Considering an infinitesimally thin cross-sectional volume, its thickness will reduce to $\mathrm{d}l$, therefore:

$$\mathrm{d}_t c_\mathrm{A} = r\,,$$

which is the *characteristic equation of the plug flow reactor*. Considering a *first-order reaction*, $-r = \kappa c_\mathrm{A}$, the concentration equation will be

$$\overline{c_\mathrm{A}} = \exp\left[-\bar{t}\right]\,.$$

2.2. **Non-ideal chemical reactors - Segregated flow analysis.** The non-ideality of industrial and natural processes led 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 ϵ, called the *exit age distribution*,

$$\epsilon[t] = \frac{c_\mathrm{A}[t]}{\int_0^\infty c_\mathrm{A}[t]\ \mathrm{d}t}\,,$$

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

$$\int_0^\infty \epsilon[t]\ \mathrm{d}t = 0\,.$$

Figure 4 shows the evolution of ϵ *vs* t. The ϵ curve is the distribution needed to account for non-ideal flow.

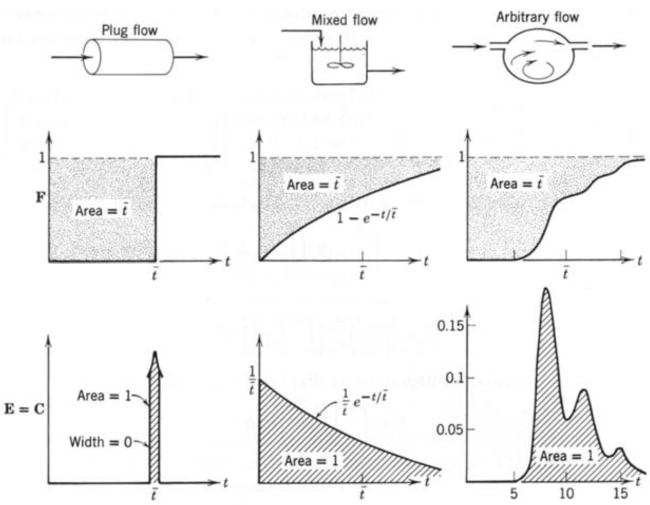

FIGURE 5. Characteristic curves for various flow types

Considering the definition of ϵ, the average residence time becomes

$$\tau_{\mathrm{h}} = \int_0^\infty t\epsilon[t]\ \mathrm{d}t\,.$$

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

$$\varphi[t] = \int_0^\infty t\epsilon[t]\ \mathrm{d}t = \frac{\int_0^{t_i} c_{\mathrm{A}}[t]\ \mathrm{d}t}{\int_0^\infty c_{\mathrm{A}}[t]\ \mathrm{d}t}\,.$$

The last equation shows that the φ curve at $t = t_i$ is defined as the cumulative area under the ϵ curve from 0 to t_i. This means that φ represents the fraction of flow with a residence time less or equal than t_i. Combining the two last equations, we have

$$\tau_{\mathrm{h}} = \int_0^1 t\,\mathrm{d}\varphi\,,$$

which is the highlighted area in fig. 5. Note that the boundaries of the last integral must be 0 to 1, since the area under the ϵ curve equals unity.

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, $\tau_{\mathrm{h}} = v/\phi_v$, 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, τ_{h} calculated in both ways will give an estimate of the dead zone volume.

Figure 5 illustrates the characteristic curves for various flows.

3. Notes on notation

3.1. **Einstein summation convention.** Consider a vector v living in three dimensional (Euclidean) space, $\mathcal{E}^3$, and consider a frame of orthonormal vectors $\{\gamma_x, \gamma_y, \gamma_z\}$ for $\mathcal{E}^3$. Let now $\{v^x, v^y, v^z\}$ be the components of v onto the frame. Then, v is traditionally written as

$$v = \gamma_x v^x + \gamma_y v^y + \gamma_z v^z\,,$$

or as in other similar fashion [2].

[2] Like the frame elements noted by e instead of γ. Moreover, in engineering, the frame would be $\left\{\hat{\imath}, \hat{\jmath}, \hat{k}\right\}$ and thus v would be written as $v = \hat{\imath}v_x + \hat{\jmath}v_y + \hat{z}v_z$. Notice the inconsistency of the engineering notation!

Consider, on the other hand, an alternative, more compact form of writing v. Begin by indexing the frame elements to $\{\gamma_i \,|\, i : 1 \to 3\}$. Then, relabel the components of v to $\left\{v^i \,|\, i : 1 \to 3\right\}$. Finally, use the summation notation to express v:

$$v = \gamma_1 v^1 + \gamma_2 v^2 + \gamma_3 v^3 = \sum_{i=1}^{3} \gamma_i v^i \,.$$

Although the summation notation helps to save typing, the Einstein summation convention goes one step further: by agreeing with dispensing with the summation sign and its limits, leaving only the indexed variables – in this case, the indexed components:

$$v = \gamma_i v^i \,.$$

Besides being more compact, the summation convention allows the expression of vectors living in any n-th dimensional space, without any notational change; *e.g.*, consider $u \in \mathcal{E}^n$ and an orthonormal frame $\{\gamma_k\}$, then the components of u on the frame can be written as

$$u = \gamma_k u^k \,,$$

where k runs from 1 to $\dim \mathcal{E}^n = n$.

3.2. **Metric.** Consider n-th dimensional Euclidean space, $\mathcal{E}^n$ and consider a frame $\{\gamma_i\}$. Then, define the *metric of* $\mathcal{E}^n$, denoted g, by the metric coefficients, g_{ij},

$$g = g_{ij} = \gamma_i \cdot \gamma_j \,.$$

For an orthonormal frame, *e.g.*, a Cartesian frame, the metric becomes Kronecker delta

$$g_{ij} = \delta_{ij} = \operatorname{diag}\left[1, 1, \cdots, 1\right] \,.$$

3.3. **Geometric derivative.** Consider n-th dimensional Euclidean space, $\mathcal{E}^n$ and consider an orthogonal frame $\{\gamma_i\}$ whose all of its elements are nonzero. Then, define a reciprocal orthogonal frame $\left\{\gamma^i\right\}$ by

$$\gamma^i = {\gamma_i}^{-1} = \frac{\gamma_i}{\gamma_i \gamma_i} \,.$$

On the other hand, define the *geometric derivative*, denoted ∇, by

$$\nabla = \gamma^i \partial_i \,,$$

where the summation convention was used.

In traditional notation, the geometric derivative would be written as

$$\nabla = \frac{\partial}{\partial \xi^i} = \partial_{\xi^i} = \partial_i \,,$$

where $\left\{\xi^i\right\}$ are the components of the position vector, ξ, on the orthogonal frame.

3.4. **Gradient.** With the geometric derivative and the summation convention, it becomes easier to note the gradient, divergence, curl and the Laplacian.

Let ϕ be a scalar field $\phi[\xi]$, then define the *gradient of* ϕ, denoted $\operatorname{grad} \phi$, by

$$\operatorname{grad} \phi = \gamma^i \partial_i \phi \,.$$

3.5. **Divergence.** Let Φ be a vector field $\Phi[\xi]$, then define the *divergence of* Φ, denoted $\operatorname{div} \Phi$, by

$$\operatorname{div} \Phi = \nabla \cdot \Phi = \gamma^i \partial_i \cdot \gamma_j \Phi^j = \gamma^i \cdot \gamma_j \partial_i \Phi^j = g^i_j \partial_i \Phi^j = \partial_j \Phi^j \,.$$

The Laplacian: let $\phi = \phi[\xi]$, then the *Laplacian of* ϕ is defined as (in Cartesian coordinates)

$$\operatorname{lap} \phi = \partial_i \partial_j \phi \,.$$