

FUNDAMENTALS OF CHEMICAL REACTOR THEORY

DIEGO HERRERA

ABSTRACT. In our everyday activities, we witness countless chemical processes, like running the washing machine or fertilizing our lawn, without looking at them with a scientific eye. However, if we were to quantify the efficiency of dirt removal in the washer or the soil distribution pattern of our fertilizer, then we would need to know which transformation the chemicals contained in those systems would undergo inside a defined volume and how fast the transformation would be.

Chemical kinetics and reactor engineering provide the scientific foundation for the analysis of most engineering processes – natural and human made. They establish the framework for the quantification of their efficiency. The theory behind chemical kinetics and reactor engineering developed into what is now known as *chemical reaction engineering*, CRE. Herein the basis of the CRE theory are presented, including some examples that will deepen the understanding of the role played by CRE as the foundation of environmental engineering.

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1. INTRODUCTION

Before beginning any calculation, a system must be clearly defined. This definition is done by drawing the *system boundaries*. If total inflows in and outflows are to be known, then a whole chemical plant is embedded by its system boundaries. Minor units, on the other hand, like unit operations, are chosen when system boundaries are drawn.

The second step is to distinguish between process and reactor calculations. *Process calculations* give an *overview* of a system, for only inflows and outflows of all mass crossing a system boundaries are used; *i.e.*, they are *black box* calculations. On the other hand, *reactor calculations* answer the question of *why* a chemical reaction occurs to a certain extent, since they are based on mass balances *and* kinetic laws. Not only does this help to design chemical reactors, but also to gain a deeper understanding of a reaction system inner workings.

Non-reactive and reactive systems: *Non-reactive systems* are systems where no chemical reaction takes place; *i.e.*, the input and output streams flowing into the system will be in the same chemical form, but perhaps in a different phase or separated from other substances. All *separation process* are examples of non-reactive systems. *Reaction systems* how to design and operate reaction systems to raw material and transformed into a chemical product of any kind; *e.g.*, microorganisms using C, N and P in wastewater for their biochemical metabolism. In chemical plants, the exact composition of both reactants and products is known, whereas in more complex systems, like an ecosystem or the atmosphere, compositions are difficult or sometimes impossible to gather.

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elements, components and inert substances. *Elements* are *conservative* within a system. They are neither consumed nor produced in a chemical process or physical separation. A *component* is a chemical compound of any kind; *e.g.*, NO_3^- , SO_4^{2-} , CO_2 and benzene. In a steady-state, in non-reactive systems, a component mass inflow equals its outflow. However, in reaction systems, equality does not hold. Finally, an *inert substance* is one that does not react, even if surrounded by reactive substances. Water, for example, is an inert substance in many systems, as it merely acts as a solvent. In other cases, the *assumption* of a substance being inert can simplify analysis, such as the case of substances that react to a small extent or is present in such large surpluses that the change in its total amount can be neglected.

2. REACTION KINETICS

Reaction kinetics is the branch of chemistry that quantifies reaction rates. But, even though this branch treats all types of chemical reactions, we limit herein the discourse to *elementary reactions* – reactions whose rates correspond to stoichiometric equations.

Consider, to begin with, a chemical process where k reactants $\{\text{R}_i \mid i : 1 \rightarrow k\}$ yield l products $\{\text{P}_j \mid j : 1 \rightarrow l\}$:



where the $\{\nu\}$ are the *stoichiometric numbers*. Then, define the *reaction rate*, r , by

$$-r = \kappa \prod_{i=1}^k \sigma_{\text{R}_i}^{\nu_i},$$

where κ is the *reaction rate coefficient*, σ_{R_i} the i -th reactant concentration and the sign is due to the fact that reactants are *consumed*. If we were, on the other hand, to express the reaction rate as a function of the products:

$$+r = \kappa \prod_{j=1}^l \sigma_{\text{P}_j}^{\nu_j}.$$

By adding the $\{\nu_i\}$, define the overall *reaction order*, n :

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

Note that $\dim n = [1]$ and that, if $\dim \sigma_{\text{R}} = [\text{N}/\text{L}^3]$ (molar concentration), then $\dim r = [\text{N}/\text{L}^3\text{T}]$. The dimensions of the rate coefficient depend on $\dim n$ and on $\dim \sigma$. If molar concentrations are used, then the rate coefficient will have the dimensions of

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

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.
- 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 as well.
- 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 °C increase in temperature, though the effect of temperature may be very much larger or smaller than this.

On the other hand, the rate coefficient depends on temperature, described by Arrhenius equation:

$$\kappa[\theta] / \kappa_0 = \exp[-e_{\text{act}}/r_{\text{gas}}\theta] ,$$

where κ_0 is the preexponential factor, e_{act} the activation energy, $[E/N]$, r_{gas} the gas constant, $[E/N\Theta]$, 8.314 462 1(75) J/mol K, and θ the thermodynamic (absolute) temperature, $[\Theta]$.

Alternatively, Arrhenius equation can be written as

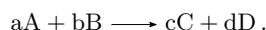
$$\kappa[\theta] / \kappa_0 = \exp[-e_{\text{act}}/k_{\text{bol}}\theta] ,$$

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

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

The dimensions of κ_0 are the same as the dimensions of κ ; *i.e.*, $\dim \kappa_0$ depend on the reaction and on the concentration.

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



Calculate the reaction rate and order.

Solution. By definition, the reaction rate is $-r = \kappa \sigma_A^a \sigma_B^b$ and order $n = a + b$.

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

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

3. MASS BALANCE

Mass is a conservative quantity, hence, given a control volume v of a system, the sum of mass flows entering the system will equal the sum exiting minus (plus) the consumed (generated) or accumulated fractions:

$$\left(\begin{array}{c} \text{rate of mass} \\ \text{in} \end{array} \right) + \left(\begin{array}{c} \text{rate of mass} \\ \text{out} \end{array} \right) + \left(\begin{array}{c} \text{rate of mass} \\ \text{produced} \end{array} \right) - \left(\begin{array}{c} \text{rate of mass} \\ \text{consumed} \end{array} \right) = \left(\begin{array}{c} \text{rate of mass} \\ \text{accumulated} \end{array} \right) .$$

The last statement represents the key point in *mass transfer*: analogously to the force balance in statics, the mass balance allows mass flow quantification and verification in chemical systems.

3.1. Ideal chemical reactors.

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

Given the reactor volume v and the initial concentration of a chemical species A, σ_{A_0} , inside the reactor, the total mass of A will be $m_A = v\sigma_{A_0}$. In the unit time, σ_A will change only by virtue of a chemical reaction. The mass balance quantifies such a change:

$$\phi_v \sigma_{A\text{in}} - \phi_v \sigma_{A\text{out}} \pm \int_v r dv = d_t m_A ,$$



FIGURE 1. Schema of a batch reactor

where r is the rate of production (+) or consumption (−) of A. Since the assumptions of no flow in or out of the reactor volume, $\phi_v = 0$, and of constant reactor volume, $dv = 0$, then the balance becomes

$$d_t m_A = d_t \sigma_A v = v d_t \sigma_A = v r ,$$

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

$$d_t \sigma_A = r ,$$

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

$$d_t \sigma_A = -\kappa \sigma_A ,$$

whose solution is

$$\sigma_A / \sigma_{A_0} = \exp[-\kappa t] ,$$

or, in alternative forms,

$$\Pi_{\sigma_A} = \exp[-\Pi_t] , \quad \text{[using dimensionless quantities]}$$

$$\overline{\sigma_A} = \exp[-\bar{t}] . \quad \text{[using scaled quantities]}$$

These expressions offer ways to relate concentration and time; *i.e.*, at any t , σ_A can be calculated given κ and σ_{A_0} .

For a *second-order reaction*¹ ($r = -\kappa \sigma_A^2$),

$$\sigma_A / \sigma_{A_0} = 1 / (1 + \kappa \sigma_{A_0} t) .$$

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

3.1.2. Continuous-stirred tank reactor. A *continuous-stirred tank reactor*, CSTR, is a well-mixed vessel that operates at *steady-state* – no mass accumulates 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 the former is not closed. Thus, the terms in the mass balance representing the mass of a species A, m_A , flowing in and flowing out will not cancel:

$$d_t m_A = \phi_v (\sigma_{A_{in}} - \sigma_{A_{out}}) + \int_v r dv = 0 .$$

Note that the inflow and outflow are equal $\phi_{v_{in}} = \phi_{v_{out}} = \phi_v$ and that the non-canceling term is the accumulation – due to the steady state hypothesis. Solving the differential equation, one finds that

$$\sigma_{A_{in}} - \sigma_{A_{out}} + \tau r = 0 ,$$

where $\tau = v / \phi_v$ is the average *hydraulic residence time*. The last equation represents the *characteristic equation for a CSTR*.

¹ The algebraic passages will hereafter be omitted.

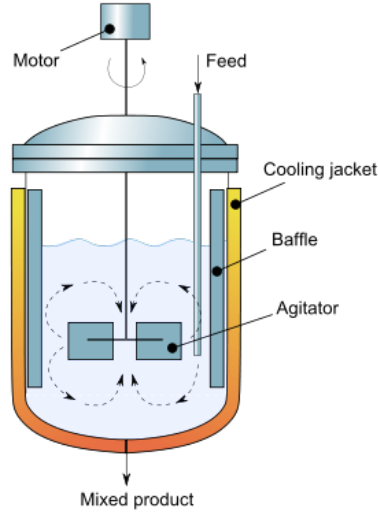


FIGURE 2. Schema of a continuous-stirred tank reactor

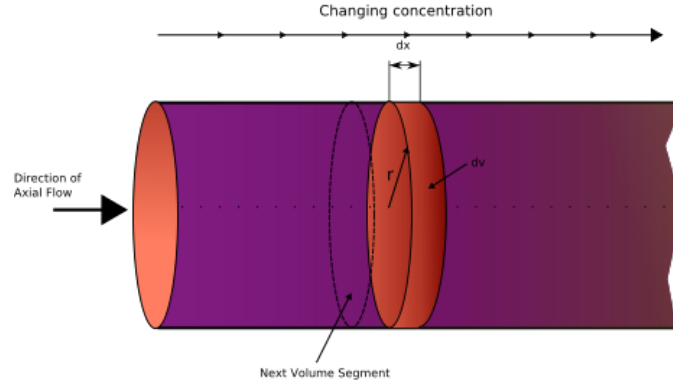


FIGURE 3. Schema of a plug flow reactor

Finally, assuming a *first-order reaction*, the model becomes

$$\sigma_{Aout}/\sigma_{Ain} = 1/(1 + \kappa\tau) \implies \Pi_{\sigma_A} = 1/(1 + \Pi_{\tau}) .$$

3.1.3. *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 every section 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

$$d_t m = \phi_v \sigma_A[t] - \phi_v \sigma_A[t + \Delta t] + \int_{\Delta v} r \, dv = 0 ,$$

hence,

$$\phi_v \sigma_A[t] - \phi_v \sigma_A[t + \Delta t] + r \Delta v = \phi_v \sigma_A[t] - \phi_v \sigma_A[t + \Delta t] + r \phi_v \Delta t = 0 \implies \frac{\Delta \sigma_A}{\Delta t} = r .$$

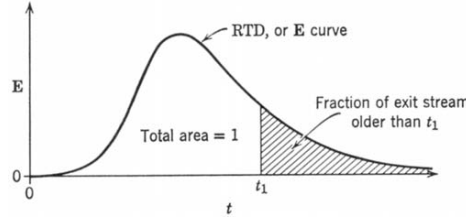


FIGURE 4. Residence time distribution: exit age distribution curve

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

$$d_t \sigma_A = r,$$

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

$$\bar{\sigma}_A = \exp[-\bar{t}].$$

3.2. 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 Ψ , called the *exit age distribution*,

$$\Psi[t] = \frac{\sigma_A[t]}{\int_0^\infty \sigma_A[t] dt},$$

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

$$\int_0^\infty \Psi[t] dt = 1.$$

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

Considering the definition of Ψ , the average residence time becomes

$$\tau = \int_0^\infty t \Psi[t] dt.$$

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

$$\Omega[t] = \int_0^\infty t \Psi[t] dt = \frac{\int_0^{t_i} \sigma_A[t] dt}{\int_0^\infty \sigma_A[t] dt}.$$

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

$$\tau = \int_0^1 t d\Omega,$$

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 Ψ 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, $\tau = v/\phi_v$, 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 calculated in both ways will give an estimate of the dead zone volume.

Figure 5 illustrates the characteristic curves for various flows.

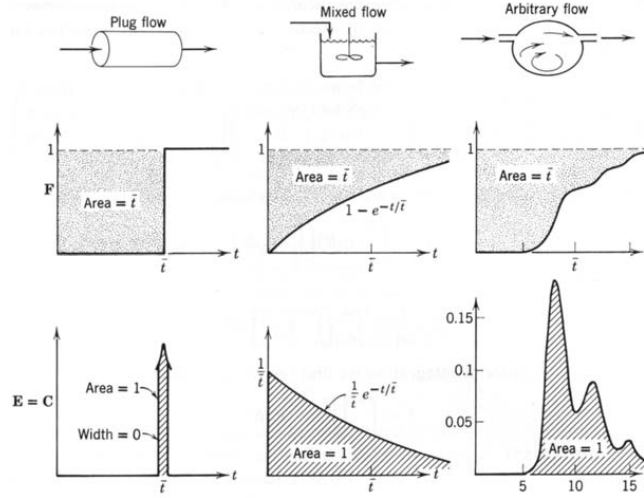


FIGURE 5. Characteristic curves for various flow types

4. 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. To motivate the treatment, consider the injection of a colored tracer into a flowing reactor: if we inject the tracer, then some of the dye will exit before the expected time (shot-circuiting), while some other will reside longer in the reactor (backmixing).

Dispersive mass flux, j_A , $[M/L^2T]$, is analogous to diffusion and can also be described using Fick's first law:

$$j_A = -\omega_A d_x \sigma_A,$$

where σ_A is the mass concentration of the species being dispersed, ω_A the dispersion coefficient, $\dim \omega_A = [L^2/T]$, and x is the position in the direction of the concentration gradient. However, dispersion differs from diffusion in that dispersion is caused by non-ideal flow patterns (*i.e.*, deviations from plug flow) – a macroscopic phenomenon, whereas diffusion is caused by random molecular motions (*i.e.*, Brownian motion) – a microscopic phenomenon. Dispersion is often more significant than diffusion in convection-diffusion problems.

In the case of a plug flow, the *dispersion model* accounts for axial (mass) dispersion, say of a species A, ω_A – the physical parameter that quantifies axial backmixing and short-circuiting of fluid. In a differential volume of flowing fluid:

$$\partial_t \sigma_A = \omega_A \text{lap} \sigma_A.$$

Considering the whole flowing fluid moving with velocity u , the last equation must be corrected for the fluid motion through the introduction of an *advection* term:

$$\partial_t \sigma_A = \omega_A \text{lap} \sigma_A - u \cdot \text{grad} \sigma_A = \omega_A \text{lap} \sigma_A - \nabla_u \sigma_A = (\omega_A \text{lap} - \nabla_u) \sigma_A,$$

where $\nabla_u \sigma_A$ is the *directional derivative of σ_A along u* .

For one dimensional flow in a Cartesian frame, the last equation can be non-dimensionalized to

$$\partial_t \sigma_A = \frac{\omega_A}{ul} \partial_{zz} \sigma_A^2 - \partial_z \sigma_A = \Pi_{pe} \partial_{zz} \sigma_A^2 - \partial_z \sigma_A,$$

where l is the reactor length and the dimensionless quantity, Π_{pe} , is called *Peclet number* – the parameter that quantifies the extent of axial. The limits of the Peclet number are

$$\Pi_{pe} = \begin{cases} \rightarrow 0 & \text{for negligible dispersion (plug flow),} \\ \rightarrow \infty & \text{for large dispersion (mixed flow).} \end{cases}$$

Figure 6 shows concentration curves in closed vessels for various extents of backmixing quantified through the dispersion model.

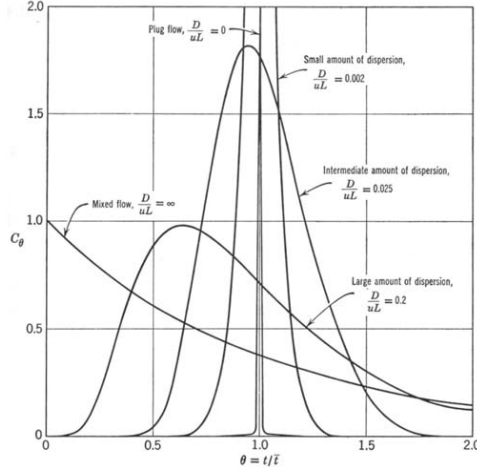
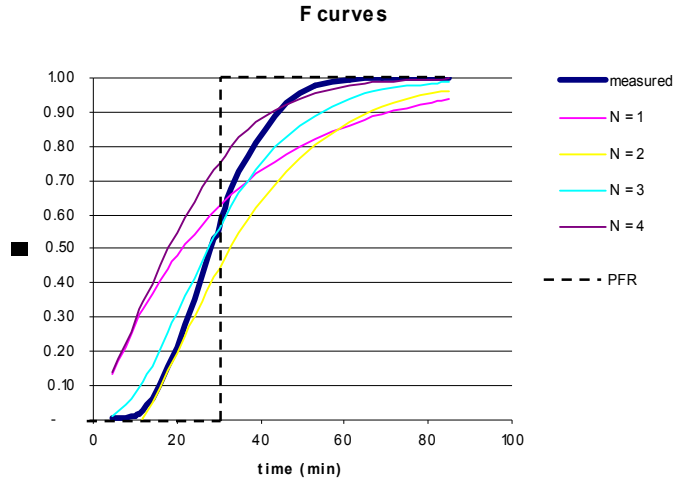


FIGURE 6. Concentration curves at different Peclet numbers

FIGURE 7. Cumulative concentration curves for different numbers of CSTR in series, where N is the number of reactors. A PFR diagram is dashed.

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 Ψ and Ω curves will be the sum of a series:

$$\Psi_k = \frac{k}{\tau} \left(\frac{kt}{\tau} \right)^{k-1} \frac{\exp[-kt/\tau]}{(k-1)!},$$

where k is the number of reactors and τ the reactor residence time, and

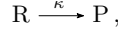
$$\Omega_k = 1 - \left(\exp[-kt/\tau] \sum_{i=1}^k \left(\frac{1}{(i-1)!} \left(\frac{kt}{\tau} \right)^{i-1} \right) \right).$$

Figure 7 visualizes this concept for the Ω curve.

5. ENERGY BALANCE

APPENDIX A. FIRST-ORDER REACTION

Consider a batch reactor hosting a first-order-kinetics chemical reaction of the form



where R represents the reactant and P the product and κ the reaction kinetic coefficient, $[1/\text{T}]$.

Let t represent the chemical reaction duration, let σ_{r} be R molar concentration and let σ_{p} be P molar concentration, $\dim \sigma_{\text{r}} = \dim \sigma_{\text{p}} = [\text{N}/\text{L}^3]$. Consider σ_{r_0} to be the reactant concentration when $t = 0$. Then, model the reaction kinetics by applying the mass conservation principle to the reactor:

$$-\text{d}_t \sigma_{\text{r}} = \kappa \sigma_{\text{r}} \quad \text{and} \quad \sigma_{\text{r}}[0] = \sigma_{\text{r}_0},$$

where the term $-\text{d}_t \sigma_{\text{r}}$ represents the reactant consumption rate, $[\text{N}/\text{T}\text{L}^3]$.

To find the reactant concentration, solve the differential equation by separating variables and applying the initial condition to have

$$\sigma_{\text{r}} = \sigma_{\text{r}_0} \exp[-\kappa t].$$

Choose the set $\{\text{N}, \text{L}, \text{T}\}$ as a dimensional system to non-dimensionalize the model by applying the scaling transformations

$$\sigma_{\text{r}} = \overline{\sigma}_{\text{r}} \sigma_{\text{r}_0}, \quad \sigma_{\text{p}} = \overline{\sigma}_{\text{p}} \sigma_{\text{r}_0} \quad \text{and} \quad \kappa t = \bar{t},$$

which yield

$$\overline{\sigma}_{\text{r}} = \exp[-\bar{t}].$$

Next, to calculate the product concentration, apply the stoichiometric condition ²:

$$\overline{\sigma}_{\text{p}} = 1 - \overline{\sigma}_{\text{r}}.$$

APPENDIX B. BATCH REACTOR

A batch reactor is a vessel characterized by:

- (1) the absence of flow: there is neither inflow nor outflow through the reactor – chemical species are placed once inside the reactor and then allowed to react; and
- (2) perfect mixing: the reactor is perfectly mixed – mass inside the reactor is perfectly distributed within it. Equivalently, it implies equal concentration in the *whole* of the reactor at a given time t ; although it changes every moment under the presence of a reaction.

Consider a batch reactor of volume v hosting a first order elementary reaction by which a reactant R yields a product P; *i.e.*, $\text{R} \xrightarrow{\kappa} \text{P}$, where κ is the reaction kinetic coefficient. Consider also that the reaction happens in a liquid. Measure concentrations on a molar basis – molar concentrations. The task is to find the reactor characteristic equation.

Write firstly the reaction rate, r , as

$$r = \kappa \sigma_{\text{R}}.$$

Since concentrations are molar, $\dim \sigma_{\text{R}} = [\text{N}/\text{L}^3]$, the reaction rate is measured volumetrically, $\dim r = [\text{N}/\text{T}\text{L}^3]$, and thus the reaction coefficient $\dim \kappa = [1/\text{T}]$.

Apply next the mass conservation law to the batch reactor – no mass flow through its boundaries:

$$\text{d}_t m_{\text{R}} = -\kappa \sigma_{\text{R}} v,$$

where the negative sign is due to the consumption of R.

According to hypothesis, the mass of R is perfectly distributed throughout the reactor, so $m_{\text{R}} = \sigma_{\text{R}} v$, and thus:

$$\text{d}_t \sigma_{\text{R}} v = -\kappa \sigma_{\text{R}} v.$$

² In dimensional form, the stoichiometric condition is $\sigma_{\text{r}} + \sigma_{\text{p}} = \sigma_{\text{r}_0}$.

But, because the reaction happens within a liquid, then $dv = 0$, that is, the reactor volume does not change (or, equivalently, the liquid is assumed to be incompressible). Then, the mass balance model changes to

$$d_t \sigma_R = -\kappa \sigma_R ,$$

which yields the characteristic equation for a batch reactor.

APPENDIX C. NOTES ON NOTATION

C.1. Einstein summation convention. Consider a vector v 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 $\{v_x, v_y, v_z\}$ 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; *e.g.*, the frame elements noted by e instead of γ ; or, as in engineering, $v = \hat{i}v_x + \hat{j}v_y + \hat{k}v_z$.

Consider, on the other hand, an alternative, more compact form of writing v . Begin by indexing the frame elements as $\{\gamma_i \mid i : 1 \rightarrow 3\}$. Then, relabel the components of v to $\{v^i \mid i : 1 \rightarrow 3\}$, where i is an index and *not* an exponent. 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 some typing, Einstein summation convention goes further: by agreeing with dispensing with the summation sign and its limits, leaving only the indexed variables:

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

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

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

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

C.2. Metric. Consider \mathcal{E}^n and a frame $\{\gamma_i\}$. Then, define the *metric of \mathcal{E}^n* , denoted g , by defining 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

$$g_{ij} = \delta_{ij} = [i = j]_{\text{iv}} = \text{diag}[1, 1, \dots, 1] ,$$

where $[i = j]_{\text{iv}}$ are Iverson brackets.

C.3. Inner product. Consider two vectors u and v in \mathcal{E}^n . Then, define the *inner product of u and v* , denoted by $u \cdot v$, by

$$u \cdot v = \gamma_i u^i \cdot \gamma_j v^j = \gamma_i \cdot \gamma_j u^i v^j = g_{ij} u^i v^j .$$

For a Cartesian frame, $g = \delta$, thus

$$u \cdot v = g_{ij} u^i v^j = \delta_{ij} u^i v^j = u^i v^j [i = j]_{\text{iv}} .$$

C.4. Partial derivatives. Consider an orthonormal frame $\{\gamma_i\}$ for \mathcal{E}^n . Then, denote the *spatial partial derivatives* by

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

where $\{\xi^i\}$ are the components of the position vector, ξ , onto the frame.

C.5. Geometric derivative. Consider \mathcal{E}^n and consider an orthonormal frame $\{\gamma_i\}$ in \mathcal{E}^n whose all of its elements are nonzero. Then, define a reciprocal orthogonal frame $\{\gamma^i\}$ by

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

Next, define the *geometric derivative*, denoted ∇ , by

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

where the summation convention was used ³.

C.6. Gradient. Let ϕ be a *scalar field* ⁴, $\phi[\xi]$, then define the *gradient of ϕ* , denoted $\text{grad } \phi$, by

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

C.7. Divergence. Let Φ be a *vector field* ⁵, $\Phi[\xi]$, then define the *divergence of Φ* , denoted $\text{div } \Phi$, by

$$\text{div } \Phi = \nabla \cdot \Phi = \gamma^i \partial_i \cdot \gamma_j \Phi^j = \partial_i \gamma^i \cdot \gamma_j \Phi^j = \partial_i g_j^i \Phi^j = \partial_i \Phi^i.$$

C.8. Laplacian. Let ϕ be a scalar field, $\phi[\xi]$, then define the *Laplacian of ϕ* , denoted $\text{lap } \phi$, by

$$\text{lap } \phi = \text{div grad } \phi = \nabla \cdot \nabla \phi = \gamma^i \partial_i \cdot \gamma^j \partial_j \phi = \partial_i \partial_j \gamma^i \cdot \gamma^j \phi = \partial_i \partial_j g^{ij} \phi.$$

Note that g cannot be factored out in front of $\partial_i \partial_j$, because g^{ij} may vary with ξ – as it's the case of spherical coordinates.

In Cartesian frames, the metric equals Kronecker delta, which does not depend on ξ , so

$$\text{lap } \phi = \partial_i \partial_j g^{ij} \phi = \delta^{ij} \partial_i \partial_j \phi = \partial_i \partial_j \phi [i = j]_{\text{iv}}.$$

C.9. Lagrangian mechanics. Lagrangian:

$$e_{\text{lag}} = e_{\text{kin}} - e_{\text{pot}}.$$

Euler-Lagrange equation:

$$d_t \partial_\xi e_{\text{lag}} - \partial_\xi e_{\text{lag}} = 0,$$

where the term $d_t \partial_\xi e_{\text{lag}}$ is called the *generalized momentum* and the term $\partial_\xi e_{\text{lag}}$ the *generalized force*.

Hamiltonian: e_{ham} .

³ In traditional notation, the geometric derivative would be written as $\nabla = \gamma^i \partial_i = \gamma^i \frac{\partial}{\partial \xi^i}$.

⁴ A scalar field is a function of the position, and possibly time, that returns a scalar.

⁵ A vector field is a function of the position, and possibly time, that returns a vector.