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 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 *italic* font.

CONTENTS

1. REACTION KINETICS

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

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

and the *reaction rate* will be defined as [1]

$$-r = \kappa c_A^a c_B^b\,,$$

where κ is referred as the *specific [per unit mass?] reaction rate coefficient*. The overall *order of reaction*, n, is defined as

$$n = a + b\,.$$

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

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

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

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[1] This is the reaction rate with respect to the reactants, the one with respect to the products being $-r = \kappa c_C^c c_D^d$.

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 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.

Given its volume v and the initial internal concentration of a species A, c_{A_0}, the total mass will be $m = vc_{A_0}$. 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:

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

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,

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

where $c_A = c_A[t]$ is the concentration at any time inside the reactor. Then,

$$\mathrm{d}_t c_A = r \,,$$

The last differential equation is the *characteristic equation* of a batch reactor. Considering a *first-order reaction*; i.e., $(r = -\kappa c_A)$:

$$\mathrm{d}_t c_A = -\kappa c_A \,,$$

whose solution is

$$\frac{c_A}{c_{A_0}} = \exp\left[-\kappa t\right] \,.$$

The last equation 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* $(r = -\kappa c_A^2)$,

$$\frac{c_A}{c_{A_0}} = \frac{1}{1 + \kappa c_{A_0} t} \,.$$

This procedure may be repeated for any order of reaction, just substituting the expression for r in the characteristic equation [9].

Note. The algebraic passages will heretofore be omitted.

2.1.2. *Continuous-stirred tank reactor.* A Continuous-Stirred Tank Reactor (CSTR) is a well-mixed vessel that operates at steady-state $(\phi_{v_{in}} = \phi_{v_{out}} = \phi_v)$. 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.

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 the mass balance will not cancel:

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

The mass balance in the last equation equals to 0, due to the *steady state hypothesis*; i.e., no mass accumulation in the reactor. Solving,

$$c_{Ain} - c_{Aout} + \tau_h r = 0 \,,$$

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,

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

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 Cartesian coordinate system subjacent $\mathcal{E}^3$. Now, let $\{\gamma_x, \gamma_y, \gamma_z\}$ be the unit vectors pointing in the directions of the Cartesian axes and $\{v^x, v^y, v^z\}$ the components of v projected onto the axes. Then, v is traditionally written as

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

Consider, on the other hand, an alternative, more compact form of writing v – the sigma notation:

$$v = \sum_{i=1}^{3} \gamma_i v^i \, ,$$

where the index i runs from 1 to 3, the dimension of space.

Einstein summation convention consists on dispensing with the summation sign and its limits, leaving only the index:

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

Geometric derivative: define the *geometric derivative*, denoted ∇, by

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

where index notation and Einstein summation convention were used.

Gradient: let $\phi = \phi\,[\xi]$, then define the *gradient of ϕ*, denoted $\mathrm{grad}\,\phi$, by

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

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

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