

# FUNDAMENTALS OF CHEMICAL REACTOR THEORY

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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.

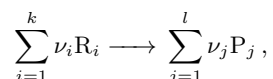
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## 1. REACTION KINETICS

*Reaction kinetics* is the branch of chemistry that quantifies rates of reaction. 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  $\{R_i \mid i : 1 \rightarrow k\}$  yield  $l$  products  $\{P_j \mid j : 1 \rightarrow l\}$ :



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

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

where  $c_{R_i}$  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  $\dim n = [1]$  and that, if  $\dim c_R = [N/L^3]$ , then  $\dim r = [N/L^3T]$ .

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.

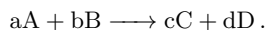
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- Concentration: reaction rate increases with concentration, as described by the rate law and explained by collision theory. As reactant concentration increases, the frequency of collision increases as well.
- Pressure: the rate of gaseous reactions 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 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 yields  $c$  moles of C and  $d$  moles of D or, symbolically,



Calculate the reaction rate and the order of reaction.

*Solution.* By definition, the reaction rate is  $-r = \kappa c_A^a c_B^b$  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  $[\text{N}/\text{L}^3]$ , then, for an order  $n$  reaction, the rate coefficient has dimensions of

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

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

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

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

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

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

Alternatively, Arrhenius equation can be written as

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

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

The difference between the two equations is the dimensions of  $e_{\text{act}}$ , because of the usage of either  $r_{\text{gas}}$  or  $k_{\text{bol}}$ : 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  $A$  are the same as the dimensions of  $\kappa$ ; *i.e.*,  $\dim A$  depend on the order of the reaction and on the concentration.

## 2. 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



FIGURE 1. Schema of a batch reactor

(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 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 the reactor volume  $v$  and the initial concentration of a chemical species A,  $c_{A_0}$ , inside the reactor, then the total mass of A inside the vessel will be  $m_A = vc_{A_0}$ . In the unit time, the concentration of A will change only by virtue of a chemical reaction. The mass balance quantifies this change in this case:

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

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

$$d_t m_A = d_t c_A v = v d_t c_A = v r ,$$

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

$$d_t c_A = r ,$$

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

$$d_t c_A = -\kappa c_A ,$$

whose solution is

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

or, in alternative forms,

$$\begin{aligned} \Gamma_{c_A} &= \exp[-\Gamma_t] && \text{[using dimensionless quantities]} \\ \overline{c_A} &= \exp[-\overline{t}] . && \text{[using scaled quantities]} \end{aligned}$$

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  $c_{A_0}$ .

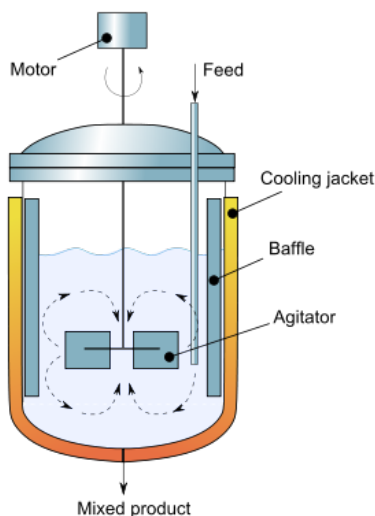


FIGURE 2. Schema of a continuous-stirred tank reactor

For a *second-order reaction*<sup>1</sup> ( $r = -\kappa c_A^2$ ),

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

This procedure may be repeated for any order of reaction 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* – 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 it is not closed. Thus, the mass of a species A flowing in and flowing out of the reactor, terms in the mass balance, will not cancel:

$$d_t m_A = \phi_v (c_{Ain} - c_{Aout}) + \int_v r dv = 0.$$

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

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

where  $\tau = v/\phi_v$  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

$$\frac{c_{Aout}}{c_{Ain}} = \frac{1}{1 + \tau}.$$

**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.

<sup>1</sup> The algebraic passages will hereafter be omitted.

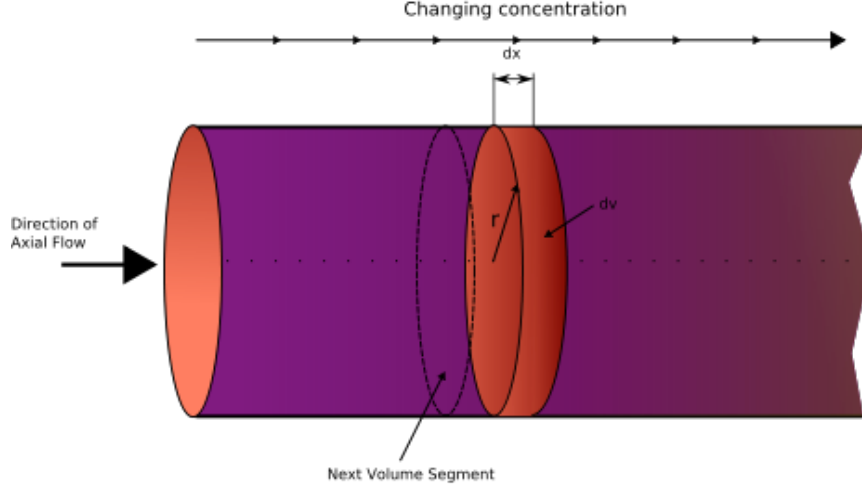


FIGURE 3. Schema of a plug flow reactor

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

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

hence,

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

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

$$d_t c_A = r,$$

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

$$\overline{c_A} = \exp[-\bar{t}].$$

**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  $\epsilon$ , called the *exit age distribution*,

$$\epsilon[t] = \frac{c_A[t]}{\int_0^\infty c_A[t] dt},$$

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

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

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

Considering the definition of  $\epsilon$ , the average residence time becomes

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

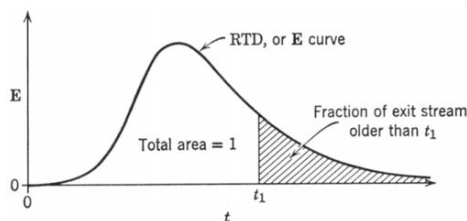


FIGURE 4. Residence time distribution: exit age distribution curve

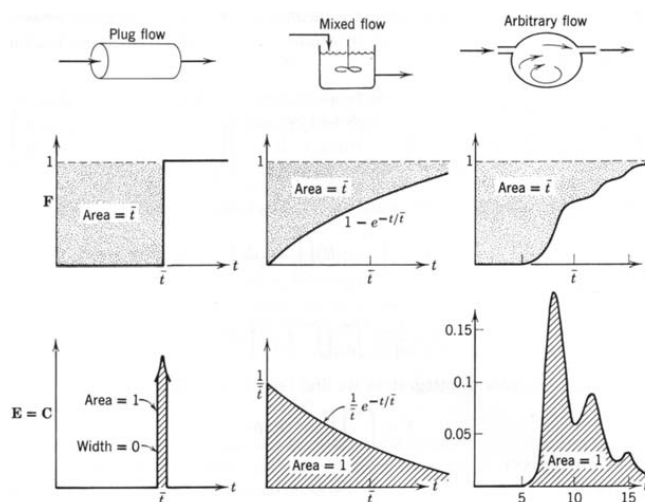


FIGURE 5. Characteristic curves for various flow types

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

$$\varphi[t] = \int_0^{\infty} t\epsilon[t] dt = \frac{\int_0^{t_i} c_A[t] dt}{\int_0^{\infty} c_A[t] dt}.$$

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

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

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  $\epsilon$  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,  $\tau$  calculated in both ways will give an estimate of the dead zone volume.

Figure 5 illustrates the characteristic curves for various flows.

### 3. 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:

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

where  $c_A$  is the mass concentration of the species being dispersed,  $A$ ,  $\sigma_A$  the dispersion coefficient,  $\dim \sigma_A = [L^2/T]$ , 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  $A$ ,  $\sigma_A$  – the physical parameter that quantifies axial backmixing and short-circuiting of fluid. In a differential volume of flowing fluid:

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

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:

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

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

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

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

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

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

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

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  $\epsilon$  and  $\varphi$  curves will be the sum of a series:

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

where  $k$  is the number of reactors and  $\tau$  the reactor residence time, and

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

Figure 7 visualizes this concept for the  $\varphi$  curve.

#### 4. NOTES ON NOTATION

**4.1. 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  $\gamma$ ; or, as in engineering,  $\{\hat{i}, \hat{j}, \hat{k}\}$ ; then,  $v = \hat{i}v_x + \hat{j}v_y + \hat{k}v_z$ .

Consider, on the other hand, an alternative, more compact form of writing  $v$ . Begin by indexing the frame elements as  $\{\gamma_i | i : 1 \rightarrow 3\}$ . Then, relabel the components of  $v$  to

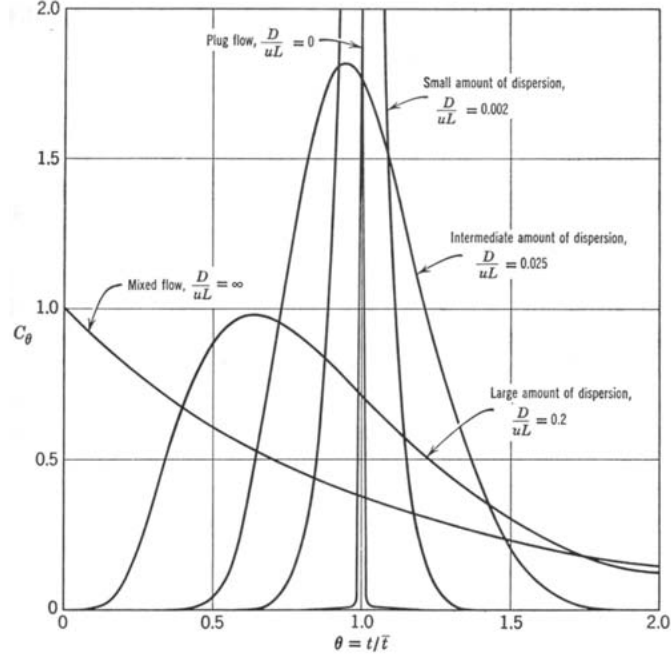
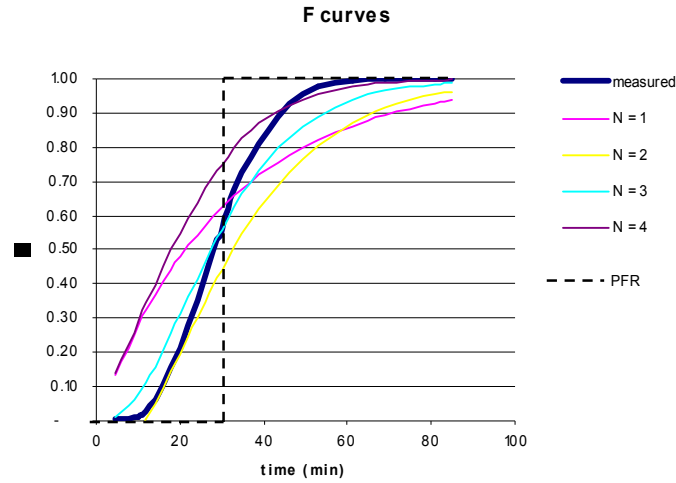


FIGURE 6. Concentration curves at different Peclet numbers

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

$\{v^i \mid i : 1 \rightarrow 3\}$ , 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, the Einstein summation convention goes 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 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  $\dim \mathcal{E}^n = n$ .

**4.2. 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.

**4.3. 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

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

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

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

**4.4. 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,  $\xi$ , onto the frame.

**4.5. 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

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

Next, define the *geometric derivative*, denoted  $\nabla$ , by

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

where the summation convention was used <sup>2</sup>.

**4.6. Gradient.** Let  $\phi$  be a *scalar field* <sup>3</sup>,  $\phi[\xi]$ , then define the *gradient of  $\phi$* , denoted  $\text{grad } \phi$ , by

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

**4.7. Divergence.** Let  $\Phi$  be a *vector field* <sup>4</sup>,  $\Phi[\xi]$ , then define the *divergence of  $\Phi$* , denoted  $\text{div } \Phi$ , by

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

**4.8. Laplacian.** Let  $\phi$  be a scalar field,  $\phi[\xi]$ , then define the *Laplacian of  $\phi$* , 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  $\xi$  – as it's the case of spherical coordinates.

In Cartesian frames, the metric equals Kronecker delta, which does not depend on  $\xi$ , so

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

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<sup>2</sup> In traditional notation, the geometric derivative would be written as  $\nabla = \gamma^i \partial_i = \gamma^i \frac{\partial}{\partial \xi^i}$ .

<sup>3</sup> A scalar field is a function of the position, and possibly time, that returns a scalar.

<sup>4</sup> A vector field is a function of the position, and possibly time, that returns a vector.

#### 4.9. 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:  $e_{\text{ham}}$ .