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NUMERICAL SIMULATION OF CONCURENT DIFFUSION AND REACTION

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SUMMARY

Mathematics and computer programming have a major contribution to chemistry. Two directions can be identified: one that searches and tries (rich) to explain the structural binding and shape of the chemical compounds [1] with major applications in QSPR/QSAR studies [2], and applied sciences such as engineering of materials and agriculture [3]; the second direction is to models the kinetic processes that are involved in chemical reactions [4]. Many such models are available here. The present paper describes the diffusion process in competition with a reaction the mathematical equations associated with them. The differential equations are numerically solves and 3D plots with MathCad program.

Keywords: diffusion, reaction, modeling

INTRODUCTION

In case of liquid phase, reactant particles must pass through solvent particles and collisions of reactants are not frequent such in gases, the mobility of them is much lower [5]. From this reason, the collision time is bigger and in this time interval of molecules contact appear the probability that the system of molecules to accumulate enough energy to react.

The molecules of reactant are permanently surround by solvent molecules and must be consider the entire energy of local assembly.

More, the molecules of solvent can active participate to reaction as intermediary catalyst of process [6, 7].

In conclusion, the global reaction process in liquids is more complex then gases [8,9].

Anyway, it can be decomposes in simple processes through establishing of a kinetic scheme [10, 11].

The general equation of diffusion written in Cartesian coordinates is (equation 1):

$$\frac{\partial \wp(x,y,z,t)}{\partial t} = K\cdot\Delta\wp(x,y,z,t) - \vec{\nabla}\left(\vec{i}+\vec{j}+\vec{k}\right)\wp(x,y,z,t)v(x,y,z,t)$$

where is assumed that diffusion are joined also by convection, which is transport of property makes through solvent movement.

The equation (1) are established based on diffusion and convection phenomena in a space region ((x,y,z),(x+dx,y+dy,z+dz)) without considering a possible reaction that can decrease or increase the value of $\wp$ property in considered space region.

A reaction is possible and is generally independent of space coordinates. Expressing his dependence, we can write (equation 2):

$$\frac{\partial \wp(x,y,z,t)}{\partial t} = +\kappa\cdot\wp^{\gamma_\wp}$$

where $\gamma_\wp$ is reaction order. Completing the equation (1) with the term from (2), it results (equation 3):

$$\frac{\partial \wp(x,y,z,t)}{\partial t} = K\cdot\Delta\wp(x,y,z,t) - \vec{\nabla}\left(\vec{i}+\vec{j}+\vec{k}\right)\wp(x,y,z,t)v(x,y,z,t) + \kappa\cdot\wp^{\gamma_\wp}$$

The equation (3), named the equation of mass balance for the property $\wp$ and is apply in numerous chemical processes.

Two such examples are the diffusion of oxygen in blood and the diffusion of a gas to the surface of a catalyst [12, 13].

The solutions of (3) equation are not easy to obtain. The equation is a inhomogeneous differential one. The analytical solving is possible only in few special cases.

For projecting of chemical reactors and kinetic biochemistry analysis that use this equation, are makes through numerical methods based on a specific real model of reaction [14].

Expressing the equation (3) in one-dimensional case without convection and with a property consume of 1 reaction order ($\gamma_{\wp} = 1$), it result (equation 4):

$$\frac{\partial \wp(x,t)}{\partial t} = K \cdot \frac{\partial^2 \wp(x,t)}{\partial x^2} + \kappa \cdot \wp(x,t)$$

If a function Q(x,t) is a solution of equation without reaction, then (equation 5):

$$\frac{\partial Q(x,t)}{\partial t} = K \cdot \frac{\partial^2 Q(x,t)}{\partial x^2}$$

and $\wp(x,t)$ are given by (equation 6):

$$\wp(x,t) = Q(x,t) \cdot e^{\kappa \cdot t}$$

is a solution of equation with reaction (equation 4).

About the equation (5) and his solution, it is completely solves using distribution theory. The general solution of (5) in $\mathbb{R}^n$ space ($x = (x_1,...,x_n)$) is (equation 7):

$$Q(x_1,...x_n,t) = \frac{1}{\left(\sqrt{4K\pi t}\right)^n} \cdot e^{-\frac{(x_1^2+...+x_n^2)}{4Kt}}$$

For n = 1 ($\mathbb{R}^1$) we obtain the solution of equation (5). Replacing in (6) this solution, it results n (equation 8):

$$\wp(x,t) = \frac{1}{\sqrt{4K\pi t}} \cdot e^{-\frac{x^2}{4Kt}} \cdot e^{\kappa \cdot t}$$

NUMERICAL MODELING

The model is bases by following equations (equation 9):

$$k := 3;\ K := 2;\ Q(x,t) := \frac{1}{\sqrt{4\cdot K\cdot \pi\cdot t}}\cdot e^{-\frac{x^2}{4\cdot K\cdot t}}$$

derived from equation (8), (equation 10):

$$zero(x,t) := K\cdot\frac{d^2}{dx^2}Q(x,t) - \frac{d}{dt}Q(x,t)$$

which plot solution for ordinary diffusion equation. Obviously, (equation 11):

$$\wp(x,t) := Q(x,t)\cdot e^{-k\cdot t}$$

For plots, we create a set of control points using two divisions, one of [0, 20] interval and other of [0, 10] (equation 12):

$$i := 0,1..20,\ j := 0,1..10$$

With this control points, the coordinate vector X and time vector T is (eq. 13):

$$X_{i,j} := \frac{i+1}{20};\ T_{i,j} := \frac{j+1}{20}$$

Vectors P and Q are calculate from (9) and (11) respectively (equation 14):

$$\wp_{i,j} := \wp(X_{i,j}, T_{i,j});\ Q_{i,j} := Q(X_{i,j}, T_{i,j})$$

Using (14), the initial and final values for property in diffusion process concurrent with reaction now can be evaluated. With constants defined in (9), values are $Q_{0,0}$ = 0.887 and $Q_{20,0}$ = 0.057. For property forming, is easy to adapt (9), putting k = -3 in place of k = 3.

PLOTS OF PROCESS EVOLUTION

Using surface plots from MathCad graphical module, graphics of property ($\wp$ or Q) dependence by space (X) and time (T) are obtained. Particular solutions of these equations are plot in figures 1 and 2 (K = 2, k = ±3):

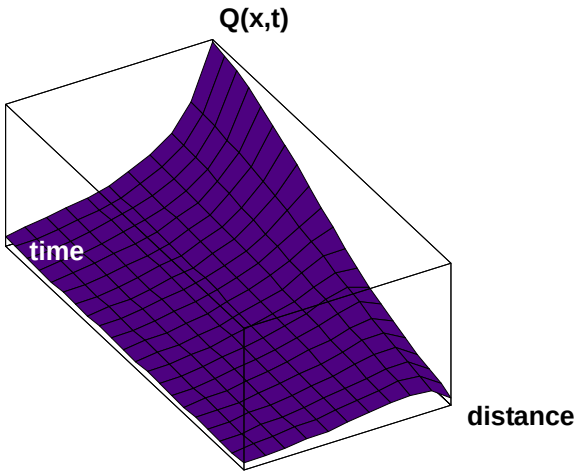

Figure 1. Space-time dependence of property $\wp$ with diffusion: solution Q(x,t) of (5) for K = 2

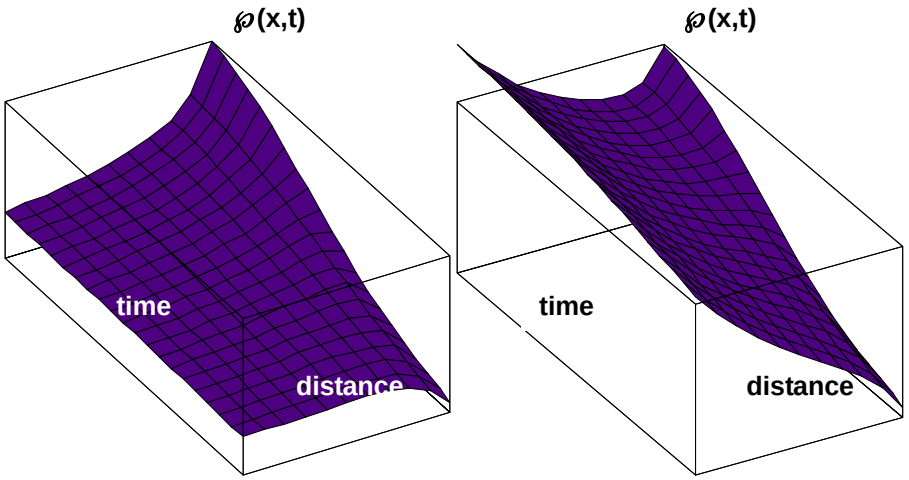

Figure 2. Space and time dependence of property $\wp$ with diffusion and property forming (κ>0 in equation 4) solution $\wp$(x,t) of (4) for K = 2 and κ = 3

and

Figure 3. Space and time dependence of property $\wp$ with diffusion and property consuming (κ<0 in equation 4) solution $\wp$(x,t) of (4) for K = 2 and κ = -3

CONCLUSIONS

The difficulty to understanding the diffusion process is primary based on his double dependency on both time and space. This article show, on one-dimensional particular case, the equations and also the 3D plots that reveal in three important cases, simple diffusion (figure 1), diffusion and producing of substance (figure 2), diffusion and consuming of substance (figure 3) respectively. Many organisms (producers, synthesizers, consumers, destroyers) have biochemical processes with one of these processes at him base mechanism to live. About numerical analysis: symbolic calculations of reaction rate for biochemical processes are, in most of cases, impossible. In opposite, the numerical modeling of biochemical kinetics proves that it is a very good instrument for mechanism understanding, comparative studies and model validation.

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