FLUID-FLUID REACTIONS: STUDY OF THE SURFACE RENEWAL THEORY IN CHEMICAL ENGINEERING COURSES

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ABSTRACT

The Surface Renewal Theory (SRT) is one of the most unfamiliar models in order to characterize fluid-fluid and fluid-fluid-solid reactions, which are of considerable industrial and academicals importance. In the present work, an approach to the resolution of the SRT model by numerical methods is presented, enabling the visualization of the influence of different variables which control the heterogeneous overall process. Its use in a classroom allowed the students to reach a great understanding of the process.

KEYWORDS: surface renewal theory, heterogeneous reactions, diffusion

Introduction

The stagnant-film, boundary-layer, and surface-renewal theories have been regarded as the cornerstone of the science of interphase mass or heat transfer in turbulent environments. The stagnant-film theory has been highly popular and remains so because of its simplicity; however, it is deemed too simplistic and unrealistic. The boundary-layer theory has been derived from a fairly rigorous and self-consistent fluid mechanical theory based on the notion of continuity; nevertheless, this theory is incapable of elucidating random disturbance or chaotic bursting at the interface under turbulent conditions. The surface-renewal theory [1, 2] has been conceived so that the deficiencies of the first two theories can be rectified through incorporation of some statistical components into the description of interphase mass or heat transport.

Numerous variants of this theory, giving rise to various mathematical models, have been proposed [3]; still the acceptance or popularity of the surface-renewal theory appears to lag behind the other two theories. This is probably attributable to the fact that the mathematical formulation of the theory is sometimes hard to understand, and is of course difficult to explain to the students.

The surface renewal theory equations

Surface-renewal theory (SRT) provides a better physical picture of mass transfer than the two-film theory, in return for a modest increase in mathematics. The model used by the SRT is shown schematically in Figure 1. The model assumes that during a fluid-fluid interaction, smal volumes or elements of the interfacial region are not static, but are constantly exchanged with new elements from a second 'bulk' region [1].
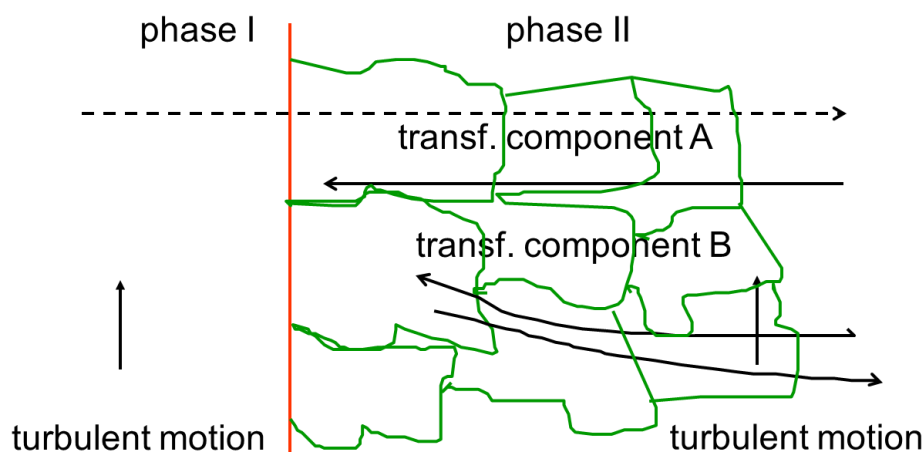

Figure 1. SRT model.

The mathematical description of this surface renewal depends on the length of time that small fluid elements spend in the interfacial region. The model assumes that the absorption profiles would depend on the time the element is in the surface, and then it needs a time distribution function of elements in the surface, Ψ (t). The product $\Psi(t)dt$ represents the fluid fraction that remains in the surface a time between 't' and 't+dt', and so:

$$\int_0^\infty \Psi(t) \cdot dt = 1$$

(1)

As the reaction rate is a function of time, the average reaction rate would be calculated as:

$$-\overline{r''}_A = \int_0^\infty -r''_A(t) \cdot \Psi(t) dt$$

(2)

where $-r''_A$ (t) is the reaction rate for an element having a residence time 't'.

SRT assumes that there is a stochastic replacement of the elements, in such a way that the probability of an element to be replaced is directly proportional to the time that the element has already been in the surface, in such a way that the distribution function is given by [1, 2]:

$$\Psi(t) = s \cdot e^{-s \cdot t}$$

(3)

where 's' represents a coeficient of replacement of the elements in the surface.
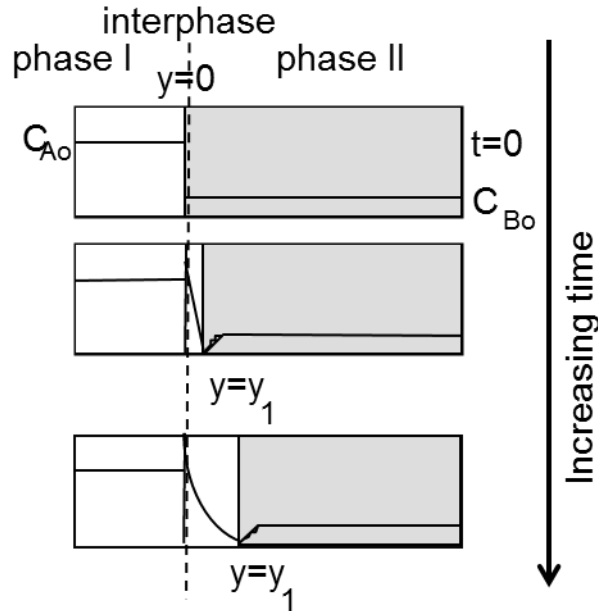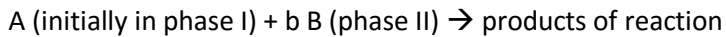
Figure 2. Evolution of the interphase and the reaction volume for an element.

Figure 2 shows the evolution of the interphase inside an element, considering the time from the moment it arrives to the surface until it is replaced.

Let us consider that the reaction takes place in such a way that:

 A (initially in phase I) + b B (phase II) → products of reaction

Inside the element and at any time 't', a mass balance of the reactant 'A' in between the interphase (y=0 in Figure 2) and the reaction plane (y = y_1 (t)) gives:

$$\frac{\partial C_A}{\partial t} = D_A \cdot \frac{\partial^2 C_A}{\partial y^2} \qquad (4)$$

A mass balance of product 'B' between y_1(t) and the bulk fluid (y=∞) would be:

$$\frac{\partial C_B}{dt} = D_B \cdot \frac{\partial^2 C_B}{\partial y^2} \qquad (5)$$

The boundary limit conditions of these two partial-differential equations are:

For A: t = 0   y > 0 $C_A = C_{A0} = 0$

t > 0   y = 0 $C_A = C_{Ai}$

$$\text{any time} \quad y = y_1 \quad C_A = 0$$

$$\text{For B:} \quad t > 0 \quad y = y_1 \quad C_B = 0$$

$$\text{any time} \quad y = \infty \quad C_B = C_{B0}$$

In the reaction plane, situated at $y_1(t)$, the concentration of the species is zero; from eqs (4) and (5), it can be shown that[1]:

$$y_1(t) = 2 \cdot \beta \cdot \sqrt{t} \tag{6}$$

where β is a constant that must be calculated. Introducing these conditions in eqs. (4) and (5) it can be obtained:

$$e^{\beta^2/D_B} \cdot erfc\left(\frac{\beta}{\sqrt{D_B}}\right) = b \cdot \frac{C_{Bb}}{C_{Ai}} \cdot \sqrt{\frac{D_B}{D_A}} \cdot e^{\beta^2/D_A} \cdot erf\left(\frac{\beta}{\sqrt{D_A}}\right) \tag{7}$$

that is a non-linear equation to be solved for β value.

On the other hand, the reaction rate at any time can be calculated by means of:

$$-r''_A(t) = -D_A \cdot \left(\frac{dC_A}{dy}\right)_{y=0} \tag{8}$$

and the average rate of reaction will be calculated using eq. (2), as already commented.

The implementation in Matlab®

Incorporating a personal computer in the classroom has brought a new quality to the study and lets teachers to easily show the influence of the different variables that affect the system behavior. Experimental results of several systems can be simulated by using the theoretical equations governing the processes, thus avoiding long and hard experimental testing that can distract the students.

From this point, the aim of this work is to provide a numerical resolution of the SRT model in order to visualize the variation of the different concentration profiles and of the rate of reaction during the whole process, in different situations. The solution of the model is achieved by a set of different Matlab® script and function files which are included as an Appendix for teachers and students.

Computer Activity for Students: Study of the Influence of Kinetic Constants and Concentration of Reactants

Let us use the finite differences method for solving equations (4)-(5). In particular we will use the explicit method. Starting on eq. (4) for C_A, each partial derivative can be expressed by:

$$\frac{\partial C_A}{\partial t} = \frac{C_{Ai}^{t+1} - C_{Ai}^t}{\Delta t} \qquad (9)$$

$$\frac{\partial^2 C_A}{\partial y^2} = \frac{C_{Ai+1}^t - 2C_{Ai}^t + C_{Ai-1}^t}{\Delta y^2} \qquad (10)$$

Substituting in eq. (4), rearranging and solving, it can be obtained:

$$C_{Ai}^{t+1} = \frac{D_A \Delta t}{\Delta y^2} C_{Ai-1}^t + \left(1 - \frac{2D_A \Delta t}{\Delta y^2}\right) C_{Ai}^t + \frac{D_A \Delta t}{\Delta y^2} C_{Ai+1}^t \quad (11)$$

that is the equation to be solved with the aid of the boundary limit conditions previously defined. It is important to note that for C_B a similar expression is obtained, starting from eq. (5).

Explicit method in the finite differences method requires, in order to assure the stability of the system, that two conditions must be satisfied. For an equation of the type:

$$C_{Ai}^{t+1} = AC_{Ai-1}^t + BC_{Ai}^t + DC_{Ai+1}^t \qquad (12)$$

those conditions are:

      1) A, B and D must be positive.

      2) The sum of the A+B+D coefficients is minor than or equal to 1.

Noticing that the coefficients A and D are always positive (in this particular case, further A=D), the remaining is to assure that B is positive, being this way if:

$$\Delta t \le \frac{\Delta x^2}{2D_A} \qquad (13)$$

On the other hand, the second condition is always true, since in this system:

$$\frac{D_A \Delta t}{\Delta y^2} + \left(1 - \frac{2D_A \Delta t}{\Delta y^2}\right) + \frac{D_A \Delta t}{\Delta y^2} \le 1 \qquad (14)$$

where it can be clearly observed that the sum always equals to unity. The same is true if the conditions are applied to C_B (equation 10) in such a way that it is also necessary that:

$$\Delta t \le \frac{\Delta x^2}{2D_B}$$

(15)

In the Matlab® code, the minimum value between (13) and (15) is chosen.

To obtain the concentration profile of C_A, equation (11) must be solved with its limit conditions and with values of the position from $y = 0$ to $y = y_i$, while for C_B its respectively limits conditions for values of the position from $y = y_i$ to $y = y_{end}$. Representing both profiles in the same graphic a form similar to Figure 2 should be obtained.

Resolution using Matlab®

Once the mathematical principles are already explained, only its implementation in Matlab® remains. For the calculation of the concentration profile, eqs. (4) and (5) must be simultaneously solved.

In the main code ('resolution.m') first the constants are defined. Then, value of β should be calculated, by solving eq. (7). For this, a Matlab® function ('betazero.m') is defined and solved in the main code.

Subsequently, the differential of position must be defined from a number of intervals and the differential of time is calculated from the stability condition. Vectors C_A and C_B are defined from the initial conditions and a *while* loop is applied from the initial to the final time to recalculate those vectors for each time, always considering the initial conditions. It must be noted that all the data about the concentrations will be stored for posterior uses. In addition, the order *drawnow* will be used, which allows the graphic visualization with time of the concentration profile.

For the calculation of the reaction rate versus time, eq. (8) must be solved. The derivate is calculated approximating to increments. Finally, the average reaction rate can be calculated for a time t according to eq. (2). For this calculation, a value of 's' in eq. (3) is needed, and the trapezoids method is used.

Results

For a given set of values of parameters C_{A0}, C_{B0} and D_A it can be calculated the C_A and C_B profiles variation with time. As an example, Figure 3 shows the results for parameters $C_{A0}=0.05$ mol/m^3, $C_{B0}=0.01$ mol/m^3, $D_A= 3 \cdot 10^{-4}$ m^2/s and $D_B=D_A/100$.

Total time is chosen in such a way that the variation of the concentration profiles is finally unapreciable, i.e., the stationary state is reached. Profiles are logically similar to those presented in Figure 2.

For this particular case we can also visualize the evolution of the reaction plane with time, given that at this position $C_A=C_B=0$. Figure 4 shows the results.
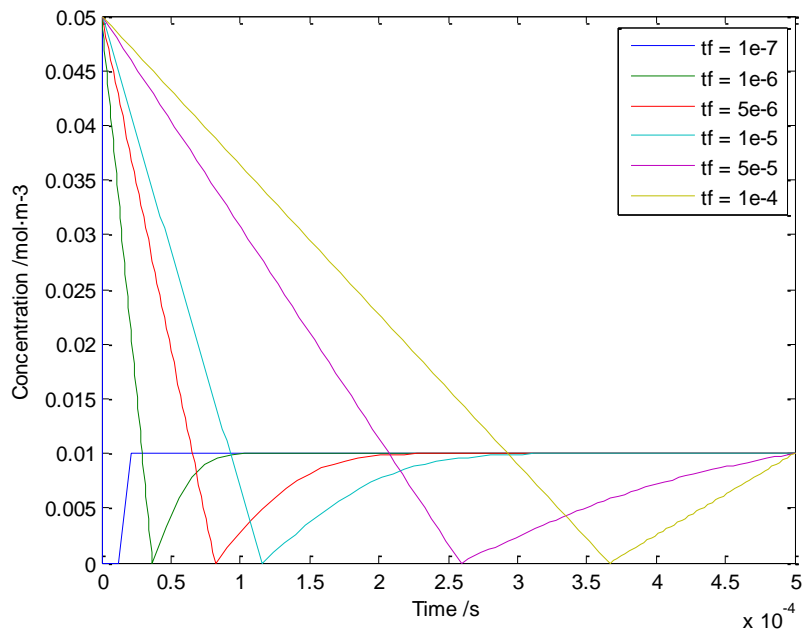

Figure 3. Variation of concentrations profiles with time in a particular case when C_{A0}=0.05 mol/m^3, C_{B0}=0.01, D_A= 3·10^{-4} m^2/s and D_B=D_A/100.
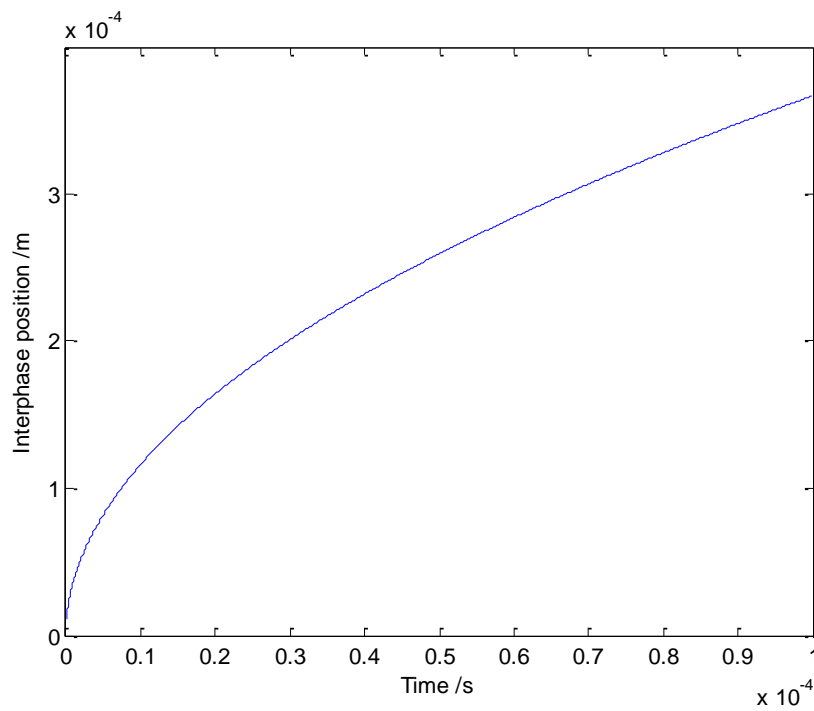
Figure 4. Evolution of the position of the reaction plane with time time in a particular case when C_{A0}=0.05 mol/m^3, C_{B0}=0.01, D_A= 3·10^{-4} m^2/s and D_B=D_A/100.
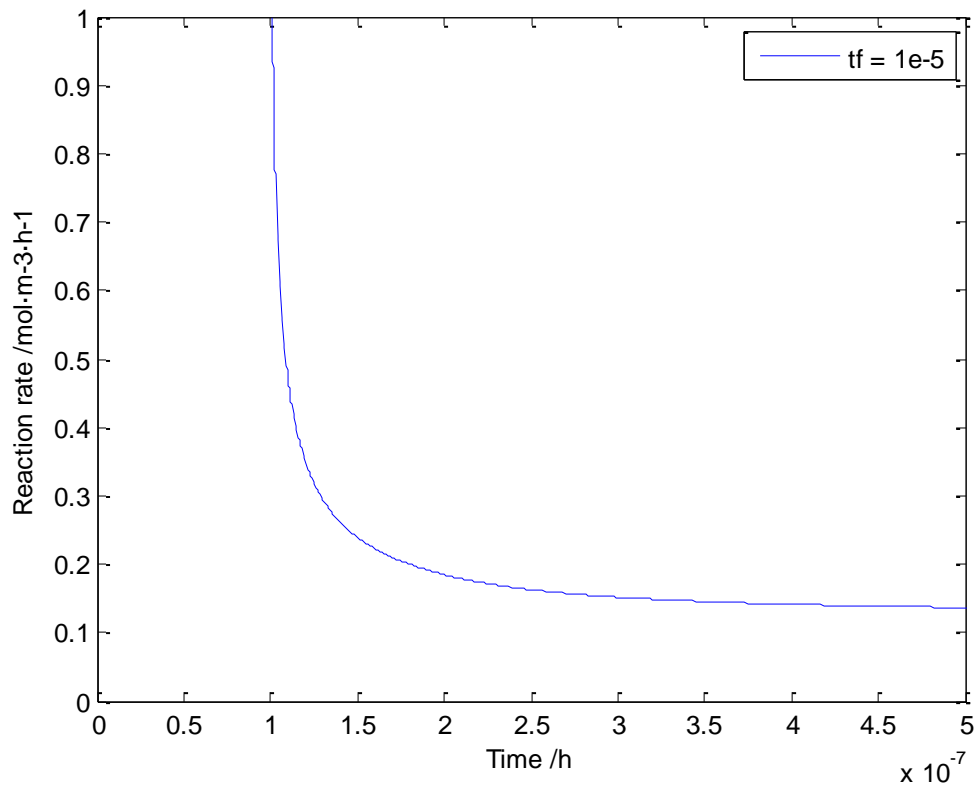

Figure 5. Reaction rate vs. reaction time in a particular case when C_{A0}=0.05 mol/m^3, C_{B0}=0.01, D_A= 3·10^{-4} m^2/s and D_B=D_A/100.

At a definite time, reaction rate can be calculated according to eq. (8). The results in this case are shown in Figure 5. It can be observed how at the beginning, when the concentration of A is low or zero, in every point except at the initial, the reaction rate is really high, while when is increasing, the reaction rate is maintained almost constant, fact that is seen at really short times. Also reaction rate is calculated according to eq. (2), and the result is 0.2095 mol m^{-3} h^{-1} (taking an arbitray value of s=10^{-3} h^{-1}).

It is even interesting to make a 3D plot of the concentrations of reactants vs. time and distance, as it is easy in Matlab®, obtaining a figure that can be even rotated. Figure 6 shows the results for this first case.
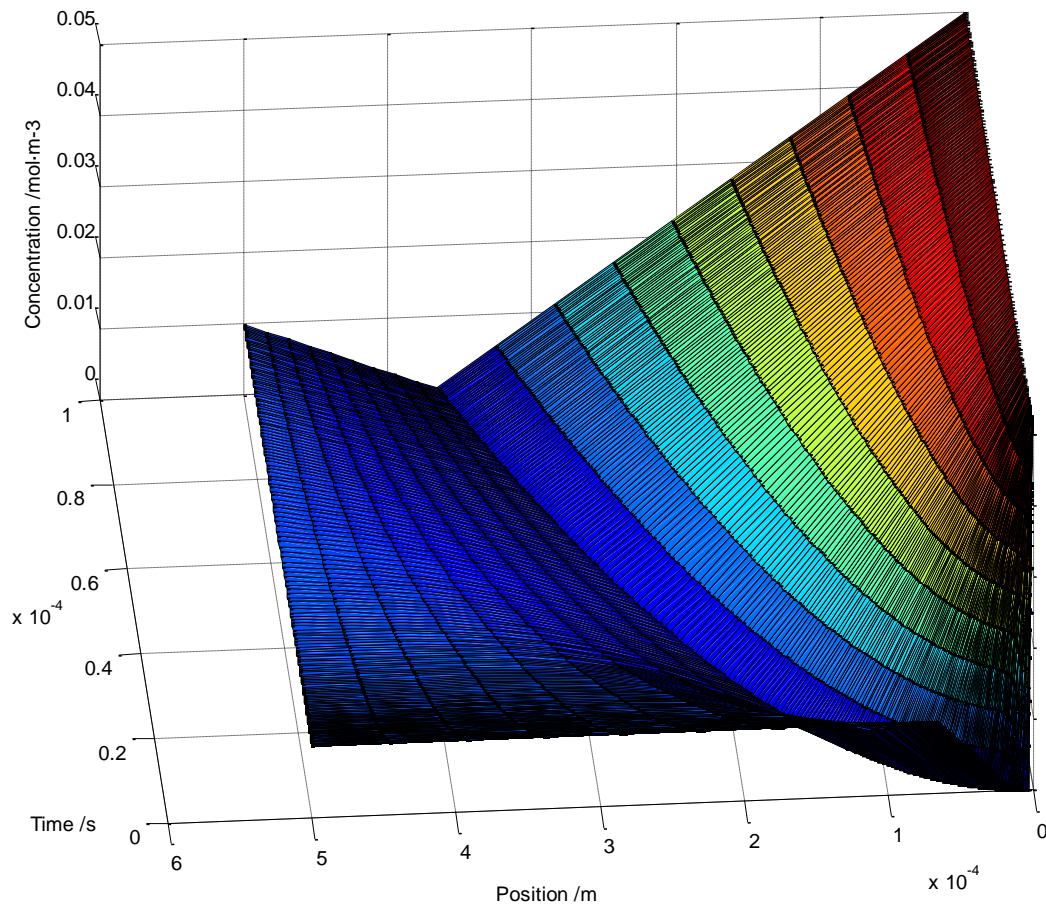
Figure 6. Evolution of the concentration profiles with time and position in a particular case when C_{A0}=0.05 mol/m^3, C_{B0}=0.01, D_A= 0.0003 m^2/s and D_B=D_A/100.

In order to visualize the effect of the difussion coeficient, let us maintain all other parameters and increase D_A to a value of 0.03 m^2/s. In that case the concentration profiles are those shown in Figure 7, where it can be observed that the stationary state is much sooner reached. In this way, the program can be used to see the effect of a variation in any parameter, as is the case of the concentrations, and obtain profiles similar to those shown in Figure 3 or 6. This would make that the students understand in a better and fliendly way the expected behaviours.
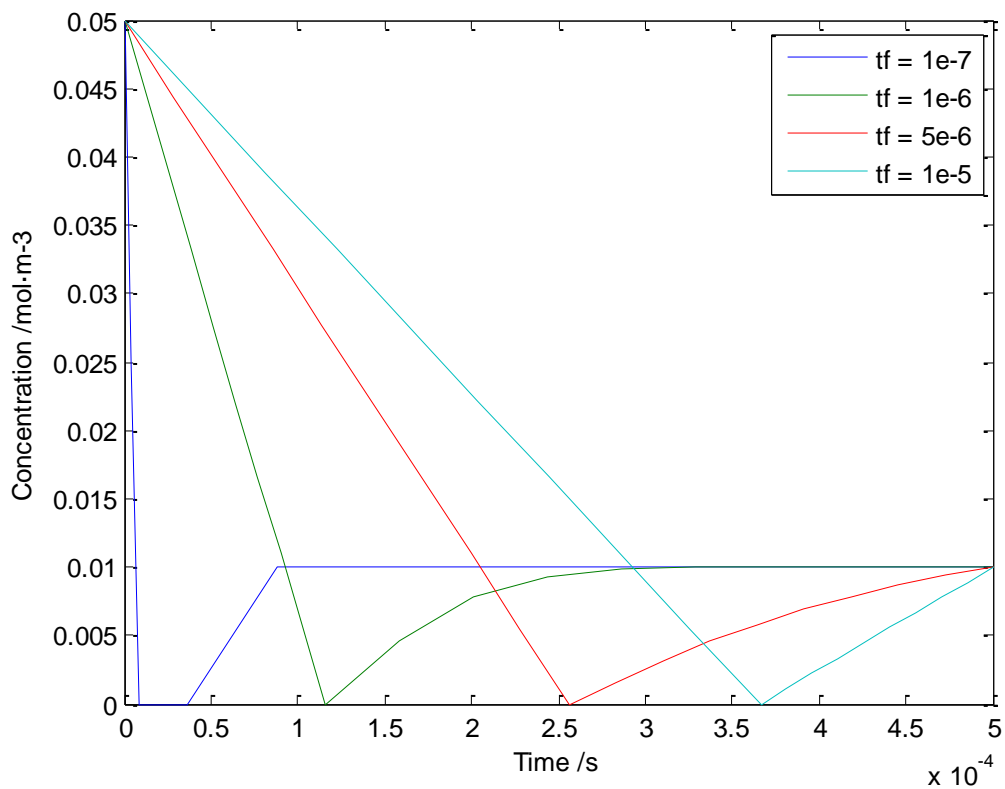
Figure 7. Variation of concentrations profiles with time in a particular case when C_{A0}=0.05 mol/m^3, C_{B0}=0.01, D_A= 0.03 m^2/s and D_B=D_A/100.

It can be noted the importance of the number of intervals when it comes to solve this problem, being really noticeable especially at the calculation of the average reaction rate. A high number of intervals offer the best solution, since the approximation of finite differences, the derivate by increments and trapezoid method would be less an approximation and more a reality, but it has a great handicap: the time of calculation. For low N values the time of resolution is really short, of few seconds, while the value of N increases, the time can reach several minutes, resulting a in hard way of working.

Conclusion

The use of personal computers in the classroom is nowadays very common and Matlab® software is helpful, easy to use and also extensively employed in many universities around the world. The SRT reaction model for fluid-fluid systems can help students to understand complicated heterogeneous processes, where the influence of many variables in the reaction rate takes place.

Using Matlab® software and a Matlab® script file, teachers have the opportunity to show the students in a very quickly and easy way how chemists can modify a reaction process with a great understanding of the influence of the reaction parameters.

Literature cited

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2. Danckwerts, P.V., *Absorption by simultaneous diffusion and chemical reaction.* Transactions of the Faraday Society, 1950. **46**: p. 300-304.

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Appendix: Matlab® codes

====================resolution.m============================

```matlab
clear all
close all
clc

global Da  Db  Cbo  Cai
tf = 1e-5; %Final time, in seconds
% CONCENTRATION PROFILE
Cai=0.05; % mol/m3, Concentration of reactant A at the interfase
Cbo=0.01; % mol/m3, Concentration of reactant B in the bulk fluid
Da=3e-3; % m2/s, Diffusivity coefficient of species A
Db=Da/100;


beta=fzero(@betazero,0.001); % Related with movement of reaction plane
yf=.0005; %m, Represents the bulk fluid
N=20; %Number of space intervals = dimension of vectors
% Initial conditions:
clear Ca Cb Can Cbn Cafinal Cbfinal yfinal yfinal1 yfinal2
t=0;
Ca=zeros(1,N);
Ca(1)=Cai;
Cb=ones(1,N)*Cbo;
Cb(1)=0;
cont=1; % Counter
t=1e-7; %Starting time, in seconds
Can=Ca;
Cbn=Cb;
while t<=tf
    y1=2*beta*(t)^0.5; % Position of reaction plane, meters
    y=linspace(0,y1,N); % Difussion zone until reaction plane
    y2=linspace(y1,yf,N); %Difussion zone from reaction plane till bulk fluid
II
```

```matlab
    Dy1=y(2)-y(1);

    Dy2=y2(2)-y2(1);

    Dt1=0.99*Dy1^2/2/Da; % Increment of time, subjected to inequality
Dt<(Dy^2/2/Da)

    Dt2=0.99*Dy2^2/2/Da; % Increment of time, subjected to inequality
Dt<(Dy^2/2/Da)

    Dt=min(Dt1,Dt2); % Lower increment of time is choosen


    for i=2:N-1

        A=Da*Dt/Dy1^2; % Coefficient

        B=1-2*A; %Coefficient

        Can(i)=A*Ca(i+1)+B*Ca(i)+A*Ca(i-1);

    end
    for i=2:N-1


        A=Da*Dt/Dy2^2; % Coefficient

        B=1-2*A; %Coefficient

        Cbn(i)=A*Cb(i+1)+B*Cb(i)+A*Cb(i-1);

    end


    Cafinal(cont,:)=Can; %Concentration of A matrix

    Cbfinal(cont,:)=Cbn; %Concentration of B matrix

    time(cont)=t; %Calculation time vector

    yfinal(cont,:)=y; %Fist half of the reaction length matrix

    yfinal1(cont)=y1; %Reaction position vector

    yfinal2(cont,:)=y2; %Second half of the reaction length matrix

    cont=cont+1;


    t=t+Dt;


    Ca=Can;

    Cb=Cbn;


    figure(1)

    plot([y y2],[Ca Cb])
```

```matlab
    xlabel('Position /m')

    ylabel('Concentration /mol·m-3')

    axis([0 yf 0 Cai])


    drawnow

end

%Reaction rate

for i=1:length(time)

    rate(i)=-Da*(Cafinal(i,1)-Cafinal(i,2))/(y(1)-y(2));

end

%Reaction rate

figure(2)

plot(time,rate)

xlabel('Time /h')

ylabel('Reaction rate /mol·m-3·h-1')

legend('tf = 1e-5')

%Reaction rate (detail)

figure(3)

plot(time,rate)

xlabel('Time /h')

ylabel('Reaction rate /mol·m-3·h-1')

legend('tf = 1e-5')

axis([0 0.5e-6 0 1])

s=1e-4; %h-1

distr=s*exp(-s*ttot); %Distribution function

%Average reaction rate

avgrate=trapz(-rate.*distr,ttot);

disp('The average reaction rate is:')

disp(avgrate)

=====================betazero.m================

function fo=betazero(x)

global Da Db Cbo Cai

fo=exp(x^2/Db)*erfc(x/Db^0.5)-Cbo/Cai*(Db/Da)^0.5*exp(x^2/Da)*erf(x/Da^0.5)
;
```