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Computer Simulation of Opposing Reaction Kinetics

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Firstly, based on the mass action law, the kinetics equation of the opposing reaction was established in the form of first-order ordinary differential equations and it was solved by the fourth order Runge-Kutta method to calculate the concentration of each substance at any time for the opposing reaction; Secondly, the equilibrium concentration of every substances can be calculated by chord secant method, the differential model of the reaction time on the change of the concentration of the substance was established and it was solved by Runge-Kutta method to calculate the equilibrium time; Finally, the software was developed by using VB programming tool and it can simulate the process of the opposing reaction in the form of graphics. The opposing liquid phase reaction was calculated and simulated as an example and the satisfactory calculation results were obtained. The software can be applied to assisted instruction in physical chemistry or chemical kinetics, and it can also be used as a calculation tool to study the opposing reaction kinetics.

1. Introduction

Opposing reaction is an important complex chemical reaction. By solving the opposing reaction kinetics equations, we may get the changes of substance concentration over time and the equilibrium time and the equilibrium concentration to provide important reference data for the design of reactors. The current physical chemistry textbooks such as Hu (2007) and Peter A (2010) prepared only give the analytical solution for a few simple opposing reaction kinetics equation through separation of variables or elimination or laplace transformation. However, most opposing reaction kinetics equations are first-order ordinary differential equations that are difficult to obtain general analytical solutions and can only obtain numerical solutions. Huang (2014), Zhong (2011), Fan (2007), Yao (2005), Dai (2007), Qi (2008), Ma (2008), Huang (2005), Qu (2011) reported the numerical simulation of the chemical reaction by Monte Carlo method or using Matlab. In this paper, the VB programming tool is used to design calculation software to calculate the opposing reaction kinetics equations and simulate the reaction process. According to the basic principle of reaction kinetics, the reaction kinetics equations are influenced by temperature, pressure, the concentration of the relevant substance and catalyst, ect; in order to simplify the model and facilitate the discussion, the opposing reaction discussed in this paper are limited to homogeneous and the reaction is carried out in a batch reactor, its reaction conditions such as temperature and catalyst are certain.

2. Building and Solving of Mathematical Model on the Opposing Reaction Kinetic

2.1 Calculation of the concentration of the substance at any time

There is an opposing reaction as follows:

$$a\mathrm{A}+b\mathrm{B}\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}c\mathrm{C}+d\mathrm{D}$$

Where k_1 and k_2 are reaction rate constants defined according to the extent of reaction. At the initial time, set the concentration of each substance as following

$$c_{\mathrm{A}}=c_{\mathrm{A}0},c_{\mathrm{B}}=c_{\mathrm{B}0},c_{\mathrm{C}}=c_{\mathrm{C}0},c_{\mathrm{D}}=c_{\mathrm{D}0} \tag{1}$$

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According to the law of mass action, we may get the following reaction rate equations:

$$v_{\mathrm{A}} = -\frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}t} = ak_1 c_{\mathrm{A}}^a c_{\mathrm{B}}^b - ak_{-1} c_{\mathrm{C}}^c c_{\mathrm{D}}^d \tag{2}$$

$$v_{\mathrm{B}} = -\frac{\mathrm{d}c_{\mathrm{B}}}{\mathrm{d}t} = bk_1 c_{\mathrm{A}}^a c_{\mathrm{B}}^b - bk_{-1} c_{\mathrm{C}}^c c_{\mathrm{D}}^d \tag{3}$$

$$v_{\mathrm{C}} = \frac{\mathrm{d}c_{\mathrm{C}}}{\mathrm{d}t} = -ck_1 c_{\mathrm{A}}^a c_{\mathrm{B}}^b + ck_{-1} c_{\mathrm{C}}^c c_{\mathrm{D}}^d \tag{4}$$

$$v_{\mathrm{D}} = \frac{\mathrm{d}c_{\mathrm{D}}}{\mathrm{d}t} = -dk_1 c_{\mathrm{A}}^a c_{\mathrm{B}}^b + dk_{-1} c_{\mathrm{C}}^c c_{\mathrm{D}}^d \tag{5}$$

We may construct a first-order ordinary differential equation system by combining Formula (1), Formula (2), Formula (3), Formula (4) and Formula (5) and calculate the concentrations of various substances at any time by solving it with the fourth-order Runge-Kutta method. The calculation steps are as follows (which was confirmed by Deng (2000), He (2001))

$$\begin{cases} c_{i,n+1} = c_{i,n} + \frac{1}{6}(k_{i1} + 2k_{i2} + 2k_{i3} + k_{i4}) \\ k_{i1} = hf_i(t_n, c_{1,n}, \cdots\cdots, c_{m,n}) \\ k_{i2} = hf_i(t_n + \frac{h}{2}, c_{1,n} + \frac{1}{2}k_{11}, \cdots\cdots, c_{m,n} + \frac{1}{2}k_{m1}) \qquad i = 1, 2, \cdots\cdots, m \\ k_{i3} = hf_i(t_n + \frac{h}{2}, c_{1,n} + \frac{1}{2}k_{12}, \cdots\cdots, c_{m,n} + \frac{1}{2}k_{m2}) \\ k_{i4} = hf_i(t_n + h, c_{1,n} + k_{13}, \cdots\cdots, c_{m,n} + k_{m3}) \end{cases} \tag{6}$$

In equation (6), *h* is the integration step, t_n represents the n^th^ time point, with the value $t_n = t_0 + nh$, and $c_{i,n}$ represents the concentration of A_i at time point t_n.

2.2 Calculation of the equilibrium concentration and the equilibrium time

When the reaction time is *t*, set the concentration of A as following

$$c_{\mathrm{A}} = c_{\mathrm{A0}} - ax \tag{7}$$

At this time, the concentration of each substance is

$$c_{\mathrm{B}} = c_{\mathrm{B0}} - bx \tag{8}$$

$$c_{\mathrm{C}} = c_{\mathrm{C0}} - cx \tag{9}$$

$$c_{\mathrm{D}} = c_{\mathrm{D0}} - dx \tag{10}$$

When the reaction reaches equilibrium, the reaction rate is zero, that is

$$v_{\mathrm{A}} = -\frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}t} = ak_1 c_{\mathrm{A}}^a c_{\mathrm{B}}^b - ak_{-1} c_{\mathrm{C}}^c c_{\mathrm{D}}^d = 0 \tag{11}$$

By putting Formula (7), Formula (8), Formula (9), Formula (10) into Formula (11), we will get

$$k_1(c_{\mathrm{A0}} - ax_e)^a (c_{\mathrm{B0}} - bx_e)^b - k_{-1}(c_{\mathrm{C0}} + cx_e)^c (c_{\mathrm{D0}} + dx_e)^d = 0 \tag{12}$$

The value of x_e in Formula (12) can be calculated by chord secant method. Put value of x_e into Formula (7), Formula (8), Formula (9) and Formula (10), we will get the equilibrium concentration of each substance.
By putting Formula (7), Formula (8), Formula (9), Formula (10) into Formula (2), we will evolve the following formulas:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1(c_{\mathrm{A}0} - ax_e)^a(c_{\mathrm{B}0} - bx_e)^b - k_{-1}(c_{\mathrm{C}0} + cx_e)^c(c_{\mathrm{D}0} + dx_e)^d \tag{13}$$

By transforming Formula (13), we will get

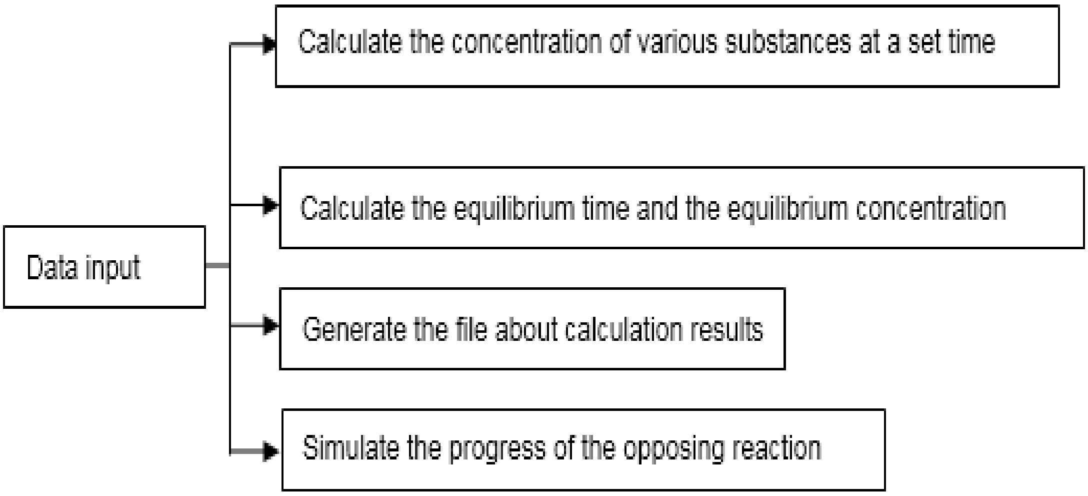
$$\frac{\mathrm{d}t}{\mathrm{d}x} = (k_1(c_{\mathrm{A}0} - ax_e)^a(c_{\mathrm{B}0} - bx_e)^b - k_{-1}(c_{\mathrm{C}0} + cx_e)^c(c_{\mathrm{D}0} + dx_e)^d)^{-1} \tag{14}$$

Under the initial conditions of t=0 and x=0, by solving Formula (14) with the fourth-order Runge-Kutta method, we can calculate the reaction time when $x = x_{\mathrm{e}}$, that is the equilibrium time.

3 Computer Simulation of Opposing Reaction Kinetics

3.1 Frame design and function introduction on the software

According to the intended function of the software, the program framework diagram is shown below:



Original data input are mainly initial concentrations of each substance, rate constant of forward reaction and reverse reaction, stoichiometric number of each substance, which also include initial time of reaction (default is 0), terminal time of reaction, and the calculation point numbers (which represents the number of calculation points between initial time and specified time, its value defaults to 1000). Click the button Calculate the button Calculate the Concentration on main interface of the software, then it can calculate concentrations of relevant substance at terminal time. Click the button Save Calculation Results to a File, then it can generate a text file, which is used to save data on concentrations of every substance vary with time. The calculation results are imported to Origin Software so that it can draw curve that concentrations of various substances change with time. Click the button Graphics Simulation, then the software will draw graph that concentrations of various substances change with time.

3.2 Realization of software function

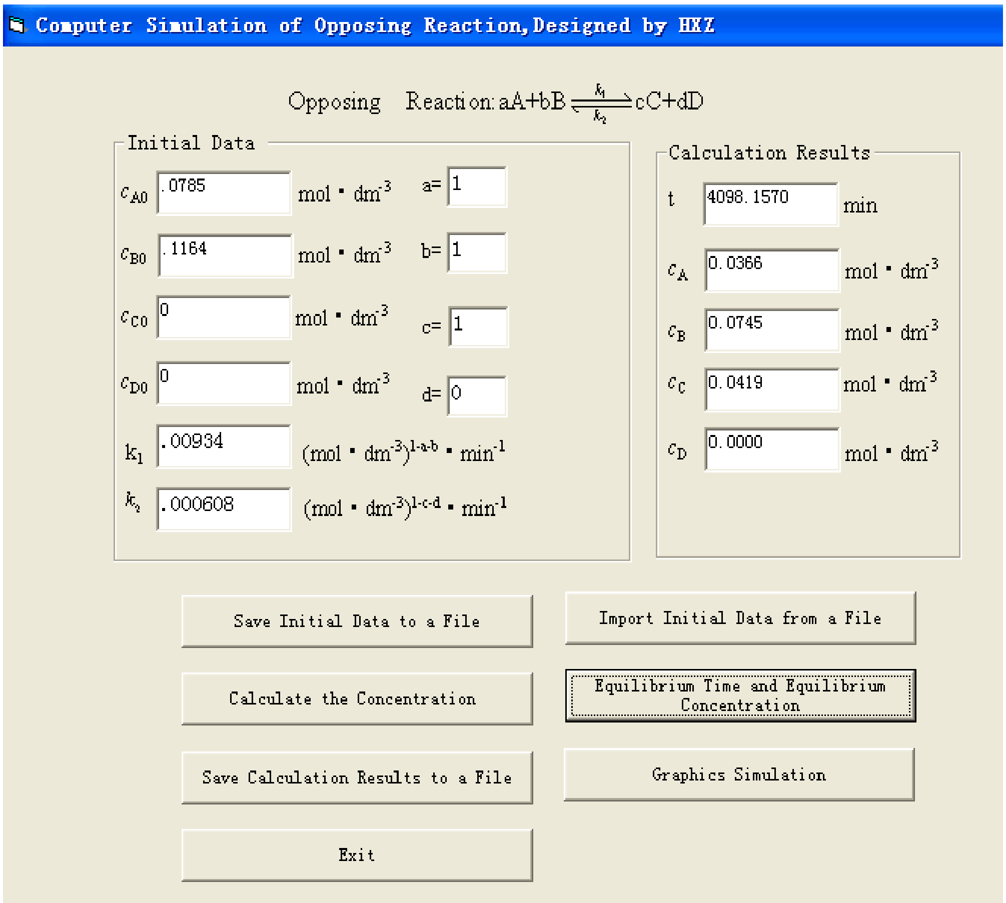
The software uses Visual Basic 6.0 as the development tool and employs modular programming technology to define the corresponding ordinary differential equations, the Runge-Kutta method and chord secant method as subprogram modules and then call subprograms to calculate the return value of $c_{i,n+1}$ according to the initial conditions of ordinary differential equations. Software drawing mainly uses “line” function to realize. Limited by the length of this paper, we do not provide detailed VB code here.

3.3 Calculation example

The liquid phase reaction in a batch reactor is as follows

$$CH_3COCH_3+HCN \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (CH_3)_2CCNOH$$

Hereinto, the initial concentrations of CH_3COCH_3 and HCN were 0.1164 and 0.0785, respectively, the rate constants of the forward and backward reactions at 15□ were $k_1 = 0.00934(\mathrm{mol}\cdot\mathrm{dm}^{-3})^{-1}\cdot\mathrm{min}^{-1}$ and $k_2 = 0.000608\,\mathrm{min}^{-1}$ respectively (The reaction rate constants were reported by Ying and Zhang (2001)). Calculate the concentrations of these substances at reaction time 73.2 minutes and the reaction reached equilibrium; simulate the reaction process.



Initial Data

c_{A0} .0785 $\mathrm{mol\cdot dm^{-3}}$ a= 1

c_{B0} .1164 $\mathrm{mol\cdot dm^{-3}}$ b= 1

c_{C0} 0 $\mathrm{mol\cdot dm^{-3}}$ c= 1

c_{D0} 0 $\mathrm{mol\cdot dm^{-3}}$ d= 0

k_1 .00934 $\mathrm{(mol\cdot dm^{-3})^{1-a-b}\cdot min^{-1}}$

k_2 .000608 $\mathrm{(mol\cdot dm^{-3})^{1-c-d}\cdot min^{-1}}$

Calculation Results

t 4098.1570 min

c_A 0.0366 $\mathrm{mol\cdot dm^{-3}}$

c_B 0.0745 $\mathrm{mol\cdot dm^{-3}}$

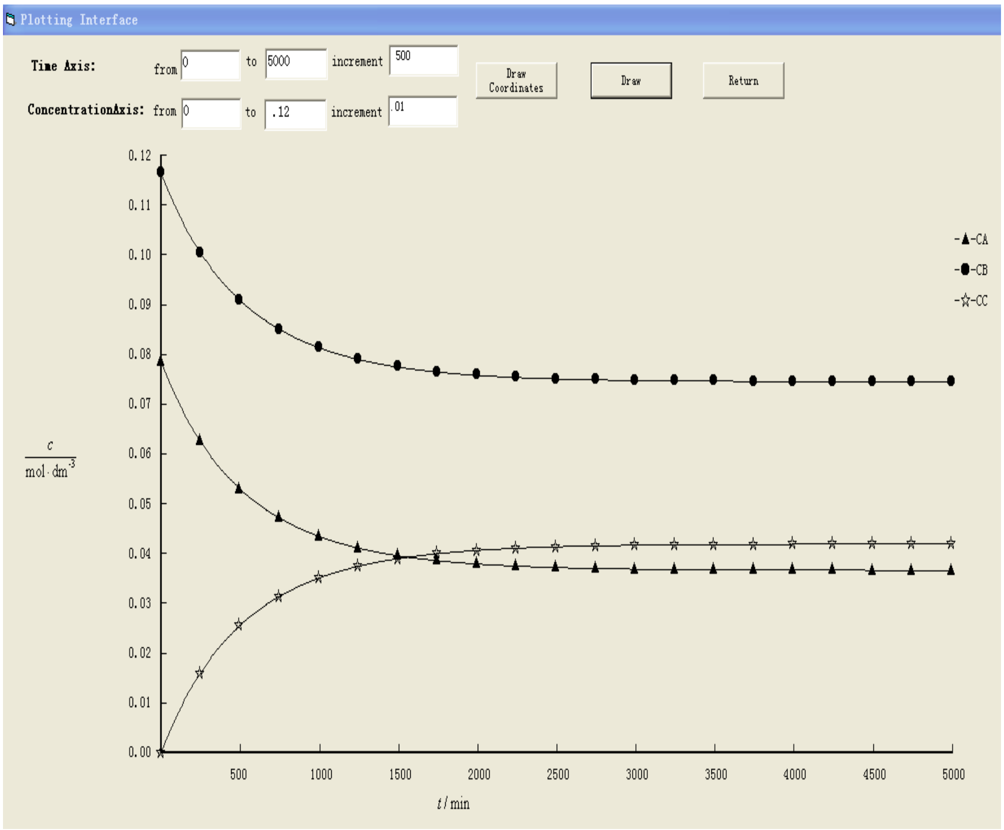
c_C 0.0419 $\mathrm{mol\cdot dm^{-3}}$

c_D 0.0000 $\mathrm{mol\cdot dm^{-3}}$

Figure 1 The main interface of the opposing reaction kinetics calculation software

For the convenience of express, A represents HCN, B represents CH3COCH3, C represents (CH3)2CCNOH. Run the software to enter into the main interface and input initial data of this reaction. Click the button Calculate the Concentration, input the reaction time 73.2 min; then the software will calculate the concentration of A at 73.2 min is 0.0728 $\mathrm{mol\cdot dm^{-3}}$. Click the button Equilibrium time and Equilibrium Concentration, then the equilibrium time and equilibrium concentration can be calculated. The main interface of the software is shown as Figure 1.

From Figure 1, when the reaction time is 4098.157min, the reaction reaches equilibrium, at this time, Click the button Graphic Simulation, then it will enter into “Plotting interface”. On this interface, set coordinate interval and calibration interval, and then click buttons of Draw the coordinate and Curve drawing separately. Graph on concentration changes of substances within 5000 minutes can be drawn. It is shown as Figure 2.



Time Axis: from 0 to 5000 increment 500

ConcentrationAxis: from 0 to .12 increment 01

Figure 2: Concentrations of each substance vs. time

The calculation results vs. the experimental results of HCN concentration are shown as Figure 3. It can be seen form Figure 3 that the calculation results agree well with the experimental results; we can conclude that the calculation results of the software are accurate and reliable.

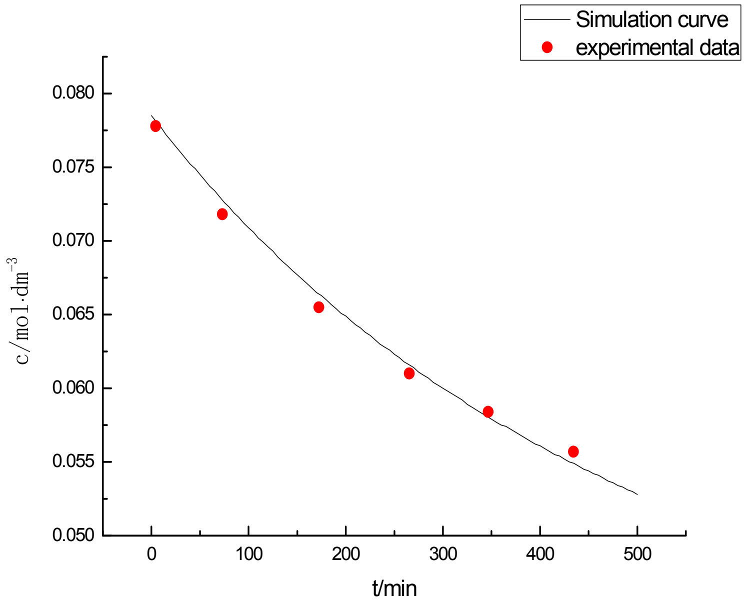


Figure 3: Concentrations- time plot for calculation and experimental data of HCN concentration

4. Conclusions

In this paper, the VB visual language programming tool and numerical calculation are used to solve the calculation problem of opposing reaction kinetics. The software may be used to predict the change trend of the concentration of opposing reacting substances over time and calculate the equilibrium time and equilibrium concentration. The software can be used as a computational tool in studying the opposing reaction kinetics; it can also assist the teaching of physical chemistry and chemical reaction kinetics, etc. to make it easy for beginners to deeply understand the characteristics of the opposing reaction through visualized computer simulation of the opposing reaction process.

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