

Solution and Computer Simulation of Complex Linear Reaction Kinetics

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Firstly, the kinetic equations of the complex linear reaction were established in the form of first-order ordinary differential equations according to the mass action law, by using the similarity transformation method of reaction rate constant matrix, the kinetic equations of the complex linear reaction were transformed from the coupling form to the uncoupled form, and the analytical solution was obtained; Secondly, the software was designed to calculate the complex linear reaction kinetics by using VB programming tool. The software can not only be used to calculate the concentration of each substance at any time for the complex linear reaction, but also has the plotting function so that it can simulate the process of the reaction vividly; In the end, the kinetics of reductive dechlorination and elimination of chlorinated ethene and 1-butene isomerization were calculated by the software, and the satisfactory results were obtained. The calculation results can guide us in the design, operation and control of the industrial device in chemical production. Software is also can be used as a computational tool in studying the kinetics of the complex linear reaction especially lumping reaction.

1. Introduction

In petrochemical engineering and petroleum refining, many chemical reactions, such as hydrogenation reactions, coal chemical industry, etc., are composed of first order or pseudo first order elementary steps and they are called complex linear reactions. The study of the kinetics of complex linear reactions has important significance to the reactor design of lumped reactions, the reaction condition control as well as higher productivity of target products (Hou et al., 2006). A large number of studies have reported the different mathematical methods to obtain the analytical solution of kinetics equations for specific types of reactions (Wei, 1962; Park, 2013; Pogliani et al., 1996; Pogliani et al., 1996; Socol, 2009; Hasan et al., 2013; Roland et al., 2016; Kyurkchiev, 2016; Nayak, 2016; Mathew and Singho, 2015; Popoola et al., 2016; Choudhury and Das, 2016; Baldyga et al., 2017; Desogus et al., 2016). The studies of linear reaction kinetics in the above mentioned literatures have all been limited to mathematical derivations; however, few studies have reported the application of computer programming to solve complex linear reaction combining with the derived formulas. This study establishes the reaction rate equation for the complex linear reactions, i.e., a first-order ordinary differential equation system; By using the mathematical method of similarity transformation for the reaction rate constant matrix, the highly coupled first-order ordinary differential equations can be transformed into the uncoupled form, thus the analytical solution of ordinary differential equations is obtained; the software is developed to solve the kinetic equation of the complex linear reaction with Visual Basic and it can vividly simulates the reaction process that the concentrations of various substances change with the time.

2. Reaction kinetic equations of complex linear reactions and its solutions

We assume that a complex linear reaction system has m substances. Set A_i as the i^{th} substance, set A_j as the j^{th} substance, set k_{ij} as reaction rate constant that Substance A_i generates Substance A_j , then any elementary reaction of the reaction system can be expressed as follows (Ying and Zhang, 2001):



Set a_i as the concentration of Substance A_i , according to the law of mass action, the reaction rate equation can be built for Substance A_i in Formula (1), which is expressed as follows:

$$\frac{da_i}{dt} = -k_{ij}a_i (i = 1, 2, \dots, m) \quad (2)$$

By establishing and integrating reaction rate equations for the elementary reactions involving the substance A_i , the reaction rate equations of substance A_i can be obtained as follows

$$\frac{da_i}{dt} = -(k_{i1} + k_{i2} + \dots + k_{im})a_i + (k_{1i}a_1 + k_{2i}a_2 + \dots + k_{mi}a_m) (i = 1, 2, \dots, m) \quad (3)$$

It can be simplified as follows:

$$\frac{da_i}{dt} = -\sum_{j=1}^m k_{ij}a_i + \sum_{j=1}^m k_{ji}a_j (i = 1, 2, \dots, m, i \neq j) \quad (4)$$

Then the kinetic equation of the complex linear reaction system can be expressed in matrix form as follows:

$$\begin{bmatrix} \frac{da_1}{dt} \\ \frac{da_2}{dt} \\ \vdots \\ \frac{da_m}{dt} \end{bmatrix} = \begin{bmatrix} -\sum_{j=1}^m k_{1j} & k_{21} & \dots & k_{m1} \\ k_{12} & -\sum_{j=1}^m k_{2j} & \dots & k_{m2} \\ \vdots & \vdots & \vdots & \vdots \\ k_{1m} & k_{2m} & \dots & -\sum_{j=1}^m k_{mj} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_m \end{bmatrix} \quad (5)$$

Set $\mathbf{a} = [a_1, a_2, \dots, a_m]^T$, $\mathbf{K} = \begin{bmatrix} -\sum_{j=1}^m k_{1j} & k_{21} & \dots & k_{m1} \\ k_{12} & -\sum_{j=1}^m k_{2j} & \dots & k_{m2} \\ \vdots & \vdots & \vdots & \vdots \\ k_{1m} & k_{2m} & \dots & -\sum_{j=1}^m k_{mj} \end{bmatrix}$, Thus the formula (5) can be simplified as follows

$$\frac{d\mathbf{a}}{dt} = \mathbf{K}\mathbf{a} \quad (6)$$

It can be seen from Formula (5) that the reaction rate of Substance A_i is not only related to the concentration of A_i , but also related to the concentrations of other substances. Formula (5) is a highly coupled rate equation system and it is difficult to find its analytic solution. If the composition vector of the reaction rate constant matrix \mathbf{K} is linearly independent, the matrix \mathbf{K} is diagonalizable (Zhang and Guo, 2009). By means of similarity transformation, the matrix \mathbf{K} can be transformed into a diagonal matrix $\mathbf{\Lambda}$ as follows

$$\mathbf{P}^{-1}\mathbf{K}\mathbf{P} = \mathbf{\Lambda} \quad (7)$$

Then $\mathbf{\Lambda} = \text{diag}(\lambda_1, \lambda_2, \dots, \lambda_m)$, The matrix \mathbf{K} can be transformed into a diagonal matrix $\mathbf{\Lambda}$ by means of similarity transformation. According to the knowledge of linear algebra, eigenvectors of matrix \mathbf{K} constitute matrix \mathbf{P} , the eigenvalues of matrix \mathbf{K} constitute the diagonal elements of matrix $\mathbf{\Lambda}$.

Formula (7) can be transformed as:

$$\mathbf{K} = \mathbf{P}\mathbf{\Lambda}\mathbf{P}^{-1} \quad (8)$$

Substitute Formula (8) to Formula (6), it can be obtained that:

$$\frac{d\mathbf{a}}{dt} = \mathbf{P}\mathbf{\Lambda}\mathbf{P}^{-1}\mathbf{a} \quad (9)$$

Formula (9) can be transformed as:

$$\mathbf{P}^{-1} \frac{d\mathbf{a}}{dt} = \mathbf{\Lambda}\mathbf{P}^{-1}\mathbf{a} \quad (10)$$

Let $P^{-1}a=q$, in which q is a $m \times 1$ matrix, by substituting it to Formula (10), it can be obtained that:

$$\frac{dq}{dt} = \Lambda q \quad (11)$$

As Λ is a diagonal matrix, Formula (11) is a reaction rate equation system in the uncoupled form, Formula (11) can also be expressed as follows:

$$\frac{dq_i}{dt} = \lambda_i q_i \quad i = 1, 2, \dots, m \quad (12)$$

By solving Formula (12) it can be obtained that:

$$q_i(t) = q_i(0) \exp(\lambda_i t) \quad i = 1, 2, \dots, m \quad (13)$$

Let $B = \text{diag}(\exp(\lambda_1 t), \exp(\lambda_2 t), \dots, \exp(\lambda_m t))$, Formula (13) can be expressed in the matrix form as follows:

$$q(t) = Bq(0) \quad (14)$$

In Formula (14), $q(0)$ represents the initial concentration vector, and $q(t)$ represents the concentration vector at Time t .

$P^{-1}a=q$, thereby $a=Pq$, When the reaction proceeds to the Time t , it can be obtained that:

$$a(t) = Pq(t) \quad (15)$$

By substituting Formula (14) to Formula (15), it can be obtained that:

$$a(t) = PBq(0) \quad (16)$$

As at the initial time, $q(0) = P^{-1}a(0)$, and by substituting it to Formula (16), it can be obtained that:

$$a(t) = PBP^{-1}a(0) \quad (17)$$

In Formula (17), $a(t)$ represents the concentration vectors of various substances at Time t , and $a(0)$ represents the concentration vectors of various substances at the initial time. According to Formula (17), the concentrations of various substances at different reaction times can be calculated.

3. Computer simulation of complex linear reaction progress

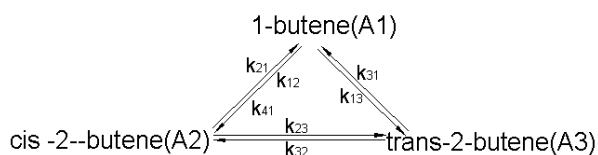
3.1 Actualization of software functions

By use of modularized programming technology, the software has been designed with Visual Basic Language. The double step QR algorithm with the origin shift is adapted to calculate the eigenvalues of the matrix K , the inverse power method to calculate the eigenvector of the matrix K , the principal Gauss Jordan elimination method to calculate the inverse matrix. All algorithms are designed as subroutines to achieve computational functions. In order to improve calculation accuracy, the data are defined as double precision. And in order to make it easy to input data, two grid controls are designed to receive the input data. Drawing is mainly realized by Line Function. Limited by the length of this paper, we do not provide detailed VB code here.

3.2 Computation examples

3.2.1 Isomerization of butenes

Butene (A_1), cis -2- butene (A_2) and trans -2- butene (A_3) can be interconverted on alumina catalyst. The relative reaction rate constants at 230°C are: $k_{12}=10.344$, $k_{13}=3.724$, $k_{21}=4.236$, $k_{23}=5.616$, $k_{31}=1.00$, $k_{32}=3.371$. Suppose at the beginning of the reaction, there is only A_1 , which initial concentration is 1.00 mol·L⁻¹, calculate the concentrations of various substances at different times of the reaction. The reaction network is indicated in the following figure.



Run the software, input initial conditions, take the reaction time as 1 and number of computation points as 100, click the **save computation result** button, the software shall instantly generate a text document to save the calculation results. The main interface of the software is shown in Figure 1. The comparison between the computation results of the software and the calculation results in the literature (Huang and Ren, 2014) is shown in Table 1.

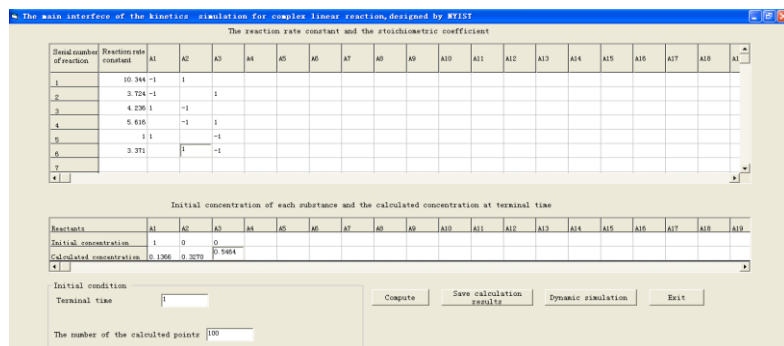


Figure 1: The main interface of the complex linear reaction kinetics software

Table 1: Comparison of calculated values and literature values

t		0.05	0.10	0.15	0.90	0.95	1.00
calculated values	[A ₁]	0.5286	0.3246	0.2321	0.1366	0.1366	0.1366
	[A ₂]	0.3034	0.3825	0.3891	0.3271	0.3270	0.3270
	[A ₃]	0.1680	0.2929	0.3788	0.5363	0.5364	0.5364
literature values	[A ₁]	0.5286	0.3246	0.2322	0.1366	0.1366	0.1366
	[A ₂]	0.3034	0.3825	0.3891	0.3271	0.3270	0.3270
	[A ₃]	0.1680	0.2929	0.3788	0.5363	0.5364	0.5364

It can be seen from Table 1 that the calculated values match into the literature values, indicating the reliability of the software computation results. The computation stability is fairly good by use of this algorithm, especially suitable in complex linear reaction systems where there are many substance species participated and many elementary reactions involved. By introducing the text document into the Origin Software, the curve of various substances concentrations in the reaction system changed with the time is shown as in Figure 2.

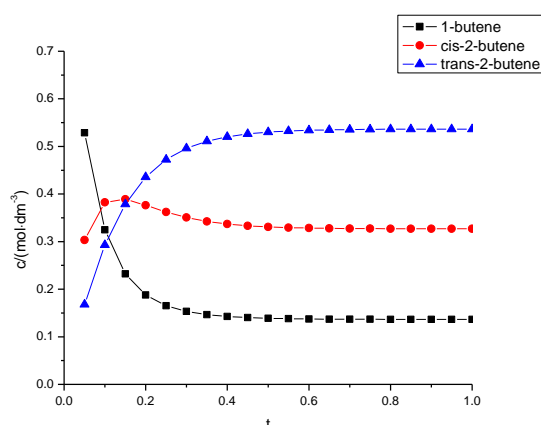


Figure 2: Concentration-time curves for isomerization reaction of 1-butene

3.2.2 Reductive dechlorination reactions of vinyl chloride

Eykholt (Eykholt et al, 1999) have proposed the reductive dechlorination reaction mechanism of vinyl chloride in the presence of zinc metal as catalyst, as shown in Figure 3.

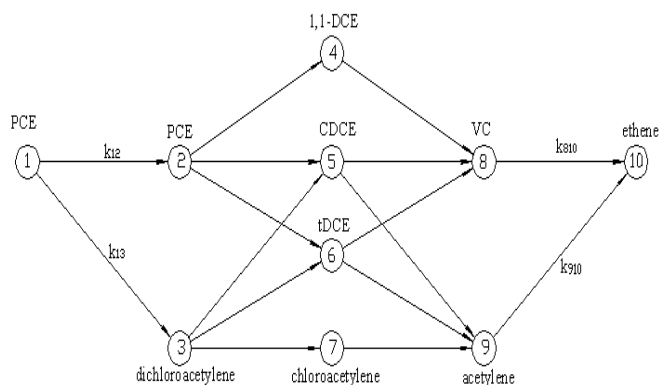


Figure 3: Mechanism for reductive dechlorination and elimination of chlorinated ethene system

(Notations: PCE: tetrachloroethylene, TCE: trichloroethylene, DCE: dichloroethylene, VC: vinylchloride)

The rate constants for each elementary reaction are as follows (which units are h^{-1}): $k_{12}=260$, $k_{13}=45$, $k_{24}=0.0681$, $k_{25}=0.603$, $k_{26}=1.47$, $k_{27}=0.943$, $k_{35}=0$, $k_{36}=20640$, $k_{37}=4430$, $k_{48}=0.0407$, $k_{58}=0.00052$, $k_{59}=0.00298$, $k_{68}=0.00064$, $k_{69}=0.0126$, $k_{78}=530$, $k_{79}=6500$, $k_{810}=0.101$, $k_{910}=0.502$. The initial concentration of tetrachloroethylene is $1\text{ mol}\cdot\text{L}^{-1}$, and the initial concentration of other substances are all 0. Simulate the reaction progress from the beginning to 100h.

Run the software, input initial conditions, the software will generate a text file to save the calculation results. By importing the text file into the Origin software, the curve of various substance concentrations in the reaction system changing with the time can be drawn, as is shown in Figure 4.

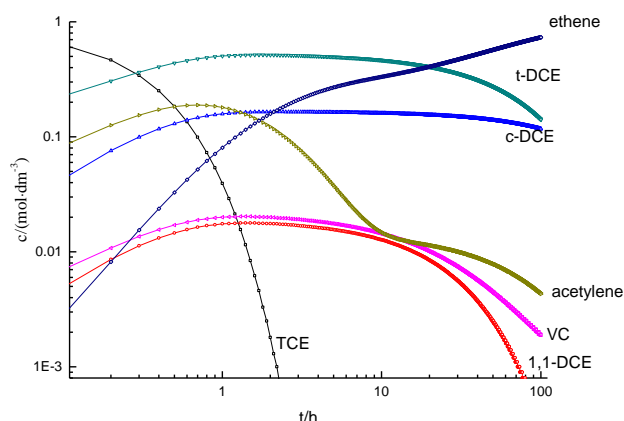


Figure 4: Concentrations of each substance vs. time for reductive dechlorination of chlorinated ethene

4. Conclusions

(1) In this paper, the reaction rate constant matrix is transformed into a diagonal matrix by calculating the eigenvalues and eigenvectors of the reaction rate constant matrix of complex linear reaction, therefore the kinetic equations of complex linear reaction are transformed from uncoupled form to uncoupled form, and the analytic solutions of complex linear reaction kinetic equations are deduced. Compared with numerical solutions, the calculation of complex linear reaction kinetics by use of the analytic solutions deduced in this paper requires only a small amount of computation work, in addition to advantages including small aggregated errors, good stability, etc.

(2) This study makes full use of the powerful computing and drawing functions of VB software, and gives the programming steps for the calculation of complex linear reaction kinetics. The software can be used as a computational tool for reaction kinetics. It can be used to study complex linear reactions, especially lumping reactions, and has a certain guiding significance for lumping reactions in chemical production.

(3) The proposed method is only applicable to the case where the reaction rate constant matrix can be diagonalizable and its eigenvalues are all real numbers whereas for the complex linear reaction kinetics where the reaction rate constant matrixes cannot be diagonalizable or the eigenvalues are not all real numbers, it is necessary to be further studied.

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