Determination of the Reaction Rate Constant for the Opposing Reaction by Integral Method

Xuezheng Huang*[a], Lei Zhang[a], Xiao Wang[b], Da Wu[a]

[a] School of civil engineering, Nanyang institute of technology, Nanyang 473004, Henan, China;
[b] Henan jiaheshengxiang Engineering consulting Co.Ltd, Zhengzhou 450012, Henan, China;
58626472@qq.com

In order to calculate the forward reaction rate constant and the reverse reaction rate constant of the opposing reaction, a calculation program was designed with VB language. According to the law of mass action, the reaction rate equation was established and it was converted into integral expression, the experimental data are calculated by using variable step size trapezoidal quadrature and least square method. The accuracy of the program in numerical simulation was verified by an example; the results show that the calculated values are in good agreement with the literature values. Inputting different parameters, the program can calculate the reaction rate of different types of the opposing reaction. It is convenient, quick and accurate to calculate the rate constant of the opposing reaction by the program. The program can be used as a tool in studying the opposing reaction.

1. Introduction

Determination of the value of the rate constant is of great importance, since it helps to determine the value of the rate of any reaction applying its rate equation. In the industrial applications of kinetics, knowledge of chemical rate equation is essential in establishing the optimum conditions of pressure, temperature, feed composition, space velocity, extent of conversion and recycling (Barraza-Burgos et al., 2015; Seoud and Abdallah, 2010). Many methods such as integral method (Mucientes, 2009; Li, 2006), differential method (Huang and Ji, 2013; Pan, 2001) half-life method (Chandran, 1999), iterative method (Li, 2011), a ratio of concentration and time method (Su, 2005) and genetic algorithm method (Shi, 2008; Abdualnaser et al, 2014; Annicchiarico et al., 2016) etc are adopted to calculate the reaction rate constant. In addition, Matlab software, Origin software and Excel software are also used to process the experiment data and determine the reaction rate constant (Asencio and Sánchez, 2002; Arlimatti et al., 2016; Xia and Tang, 2009; Hernández & Ruiz, 1998; Seoud & Abdallah, 2010). Several simulation programs were developed to determine the reaction rate constant and the satisfactory results have been obtained (Adam and James, 2006, Seoud and Abdallah, 2010). The kinetic rate constants for many forms of complex reactions have been studied and reported, such as consecutive first-order reaction (Li, 2011; Erdoğdu and Şahmurat, 2007; Pedrazzi et al., 2012; Gagliano et al., 2016), consecutive and parallel reactions both with a reversible first step (Ser and Jun, 2015), parallel - consecutive second order reaction (Chischova and Alzaydien, 2009), competitive consecutive second-order reactions (Mcmillan, 2002), consecutive second-order reaction (Yao and Wang, 2005), irreversible two-step consecutive reaction (Gábor, 2015), etc. However, the study on the calculation of the opposing reaction rate has not yet been reported. This paper uses knowledge of reaction kinetics to deduce the calculation formula of the reaction rate constant of opposing reaction as well as adopts integral method and least square method to calculate and solve the reaction rate constants.

2. Calculation basis of the reaction rate constants of opposing reaction

Suppose that a certain opposing reaction is as follows

$$a\mathrm{A} + b\mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} c\mathrm{C} + d\mathrm{D}$$
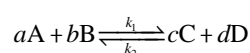
Among them, k_1, k_2 are reaction rate constants which are defined according to the extent of the reaction. The concentration of each substance at the initial moment of the reaction, which means $t=0$, is measured as follows

$$c_A = c_{A0}, c_B = c_{B0}, c_C = c_{C0}, c_D = c_{D0} \tag{1}$$

Suppose that the reaction progresses to t moment, the concentration of A is measured to be c_A, set

$$x = (c_{A0} - c_A)/a \tag{2}$$

Thus when t=t, the concentration of each substance can be described as follows

$$c_A = c_{A0} - ax, c_B = c_{B0} - bx, c_C = c_{C0} + cx, c_D = c_{D0} + dx \tag{3}$$

According to mass action law, the reaction rate expression of A is

$$v_A = -\frac{dc_A}{dt} = ak_1 c_A^a c_B^b - ak_2 c_C^c c_D^d \tag{4}$$

Substitute equation (3) into equation (4), we can get

$$\frac{dx}{dt} = k_1(c_{A0} - ax)^a(c_{B0} - bx)^b - k_2(c_{C0} + cx)^c(c_{D0} + dx)^d \tag{5}$$

When opposing reaction reaches equilibrium, the concentration of each substance can be described as follows

$$c_A = c_{Ae} = c_{A0} - ax_e, c_B = c_{Be} = c_{B0} - bx_e, c_C = c_{Ce} = c_{C0} + cx_e, c_D = c_{De} = c_{D0} + dx_e \tag{6}$$

In equation (6), c_{Ae} c_{Be}, c_{Ce}, c_{De} are the concentrations of each matter when the reaction reaches equilibrium. Because when the reaction reaches equilibrium, v_A=0, from equation (4), we can get

$$k_1 c_{Ae}^a c_{Be}^b = k_2 c_{Ce}^c c_{De}^d \tag{7}$$

According to the definition of equilibrium constant and equation (6), we can get

$$K = \frac{c_{Ce}^c c_{De}^d}{c_{Ae}^a c_{Be}^b} = \frac{k_1}{k_2} \tag{8}$$

Substitute equation (8) into equation (5), we can get

$$\frac{dx}{dt} = k_1[(c_{A0} - ax)^a(c_{B0} - bx)^b - \frac{1}{K}(c_{C0} + cx)^c(c_{D0} + dx)^d] \tag{9}$$

Equation (9) can be denoted as

$$\frac{dx}{dt} = k_1 f(x) \tag{10}$$

Thus $f(x) = (c_{A0} - ax)^a(c_{B0} - bx)^b - \frac{1}{K}(c_{C0} + cx)^c(c_{D0} + dx)^d$, equation (10) can be transformed by integration as follows

$$\int_0^x \frac{dx}{f(x)} = k_1 t \tag{11}$$

If there are m groups of experiment data of concentration of A in this opposing reaction and their time points are respectively $t_1, t_2, \ldots t_m$, the concentrations of A which correspond to each time point are measured to be $c_{A1}, c_{A2}, \ldots c_{Am}$ respectively, among above, t_1=0 to indicate the initial time of the reaction. Correspondingly, the values of x_i at each time point of the reaction can be calculated from equation (2) and the concentration of A c_{Ae} at the time point $t=\infty$ when the reaction reaches equilibrium also can be measured. Then the concentrations of B, C and D c_{Be}, c_{ce} and c_{De} when the reaction reaches equilibrium can also be calculated from equation (2) and equation (3). Then c_{Be}, c_{Ce} and c_{De} can be substituted into equation (8) to calculate the equilibrium constant k of this reaction, which can be substituted into equation (11) to participate in integration

calculations. Set $y_i = \int_0^{x_i} \dfrac{dx}{f(x)}$, the value of y_i can be calculated by variable step size trapezoidal quadrature.

This method calculates relevant integration value by decreasing the integration step size by half each time until the difference between two adjacent integration is less than assigned error. At this moment, the calculation can be stopped, which increases the accuracy of integration calculation. The detailed calculation procedures are as follows (Deng, Ge and Cheng, 2000).

Divide the integration internal [0, x_i] equally with an interval of 2^{n-1} and the corresponding trapezoidal integration formula is

$$S_n = h_n[\frac{1}{2}\frac{1}{f(0)} + \frac{1}{2}\frac{1}{f(x_i)} + \sum_{k=2}^{2^{n-1}}\frac{1}{f(x_k^{(n)})}] \tag{12}$$

In equation (12), $h_n = (x_i - 0)/2^{n-1}$, $x_k^{(n)} = 0 + (k-1)h_n, k = 1,\cdots.2^{n-1}+1, n = 1,2,\cdots$ while the calculation formula of S_{n+1} is as follows

$$S_{n+1} = h_{n+1}[\frac{1}{2}\frac{1}{f(0)} + \frac{1}{2}\frac{1}{f(x_i)} + \sum_{k=2}^{2^n}\frac{1}{f(x_k^{(n)})}] \tag{13}$$
$$x_{2k-1}^{(n+1)} = x_k^n, k = 1,2,\cdots,2^{n-1}+1$$

Combine equation (12) and equation (13), we can get

$$S_{n+1} = \frac{1}{2}[S_n + h_n\sum_{k=1}^{2^{n-1}}\frac{1}{f(x_{2k}^{(n+1)})}] \tag{14}$$

When $abs(S_{n+1} - S_n) < \varepsilon S_n$ (ε is assigned error limit), the integration calculation can be stopped. At this moment, we can select $y_i = S_{n+1}$.

As it can be known from equation (11), y_i and t_i assume linear regression relationship. Their slope is the reaction rate constant of forward reaction -k_1, which can be calculated by least-square method. The specific calculation procedures are as follows.

Set the mean-square error- $Q = \sum_{i=1}^n (y_i - k_1 x_i)^2$, thus when $\dfrac{\partial Q}{\partial k_1} = -2\sum_{i=1}^n (y_i - k_1 x_i)x_i = 0$, Q is the minimum. Therefore the calculation formula of k_1 can be deduced as follows

$$k_1 = \sum_{i=1}^m x_i y_i \bigg/ \sum_{i=1}^m x_i^2 \tag{15}$$

The values of the reaction rate constant of backward reaction -k_2 can be calculated from equation (8)

$$k_2 = k_1/K \tag{16}$$

3. Program design

The program is designed in Visual Basic language and adopts modular programming technologies to design a customized subprogram-integral which can calculate the integration by variable step size trapezoidal quadrature. The customized parameters of the subprogram-integral include the upper limit and the lower limit of the integration internal and the returned parameters are integration values. For the convenience of data input, the program covers a floating textbox on the current unit of grid flex control in order to facilitate the input of data. The users can also import data from the external data file to input initial data. The flowchart of the program is demonstrated in Figure 1. Limited by the length of this paper, this paper doesn't provide the detailed VB codes, the codes of the algorithm of trapezoidal integration can be found in the literature (He, 2001).
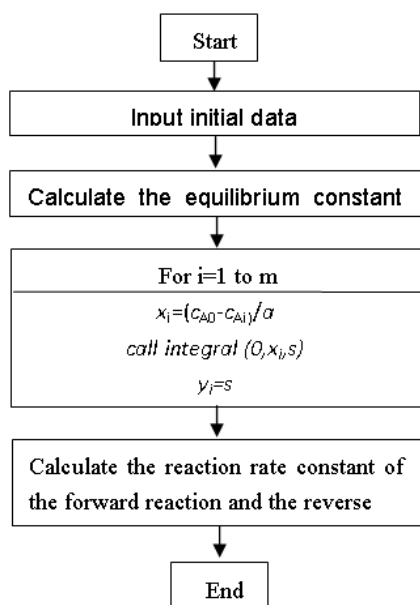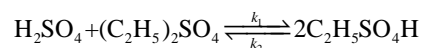
Figure 1: Flow chart of the VB program algorithm.

4. Calculation examples

The sulphuric acid and the diethyl sulfate react in water according to following formula:

$$H_2SO_4+(C_2H_5)_2SO_4 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2C_2H_5SO_4H$$

The initial concentrations of the sulphuric acid (A) and diethyl sulfate (B) are both 5.50 mol·dm^{-3}. At the temperature of 22.9°C, At 22.9°C, the experimental data is shown in Table 1, determine the reaction rate equation of the reaction.

Table 1: The concentration vs. time for sulphuric acid

t/min	0	41	48	55	75	96	127	146	162
c_A/ mol·dm^{-3}	5.500	4.910	4.810	4.685	4.380	4.125	3.845	3.620	3.595
t/min	180	194	212	267	318	368	379	410	∞
c_A/ mol·dm^{-3}	3.445	3.345	3.275	3.070	2.925	2.850	2.825	2.790	2.600

Use A to represent H_2SO_4, use B to represent $(C_2H_5)_2SO_4$, use C to represent $C_2H_5SO_4H$, thus the reaction can be represented as $A+B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2C$, which belongs to 2-2 order opposing reaction.

Run the program, input the concentration of A at corresponding time point and input the equilibrium concentrations and the stoichiometric numbers of A, B and C, press the button calculates the reaction rate constant and the reaction rate constants of forward reaction and reverse reaction can be calculated to be 6.68×10^{-4}s^{-1} and 1.34×10^{-5} s^{-1} respectively, which are relatively close to the reference values- $k_1 = 6.775 \times 10^{-4} s^{-1}, k_2 = 1.361 \times 10^{-4} s^{-1}$ (Zhong, 2011). The program interface is demonstrated in Figure 2.
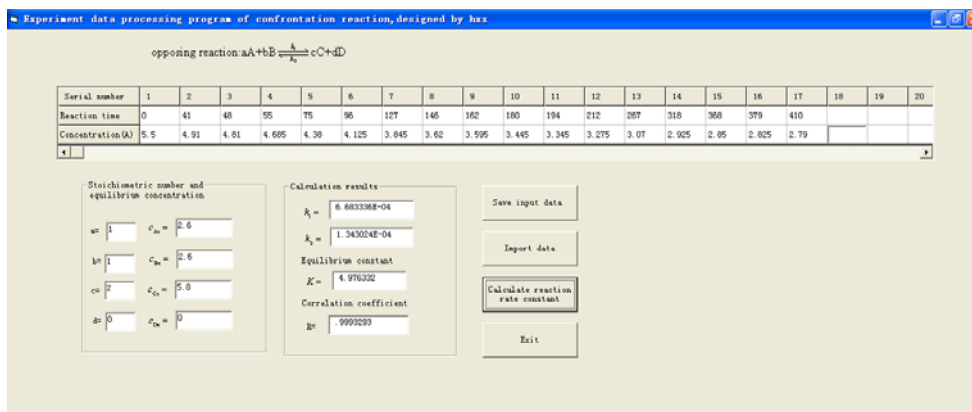
Figure 2: The main interface of the program.

The numerical simulation of this reaction can be carried out based on the reaction rate constant obtained from the program. The concentration calculation curve and can experimental data of A at 22.9°C are demonstrated in Figure 3. From Figure 3, the calculation values agree well with the experimental values, which indicates that the reaction rate constant determined by the program are in good agreement with experimental data at 22.9°C.
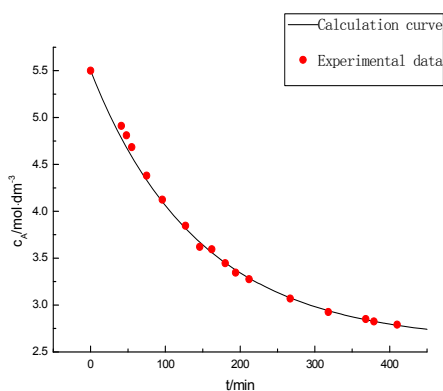

Figure 3: Comparison of the experimental and calculation data

4. Conclusions

It takes a heavy workload to process the kinetic experiment data of opposing reaction, especially when the data are in large amounts; manual calculation is not only squandering time and vigor, but also is easy to make mistakes. The data processing program of this research has a friendly interface and convenient input. Additionally, inputting different stoichiometric coefficient, the program can calculate the forward reaction rate constant and reverse reaction rate constants of the opposing reactions accurately and quickly. The kinetic parameters calculated by the program can be used to simulate the reaction progress of the opposing reactions. The kinetic of the reaction can be studied by comparing the simulation curve and the experiment curve to explore the reaction mechanism of the reaction.

Acknowledgments

Reference

Abdualnaser M., Hatami T., Glisic S.B., 2014, Determination of kinetic parameters for complex transesterification reaction by standard optimisation methods, Hemijska Industrija, 68, 2, 149-159. doi: 10.1063/1.1630798.

Annicchiarico A., 2016, A structural shape optimization approach using flexible distributed evolution principles. Revista de la Facultad de Ingeniería, 31, 2, 46-65. Doi: 10.21311/002.31.2.02

Arlimatti S., Hassan S., Habbal A., 2016, Minimization of Communication Cost between Controller Domains with Graph Partitioning Algorithms. Revista de la Facultad de Ingeniería, 31, 5, 01-08. Doi: 10.21311/002.31.5.01

Barraza-Burgos J.M., García-Saavedra E.A., Chaves-Sanchez D.b., Trujillo-Uribe M.P., Velasco-Charria F.J., Acuña-Polanco J.J., 2015, Thermogravimetric characteristics and kinetics of pyrolysis of coal blends. Revista de la Facultad de Ingeniería, 30, 4, 17-24.

Chandran P., 1999, A simple method for the calculation of rate, order and rate constant of a chemical reaction, International Amateur-Professional Photoelectric Photometry Communications, 75, 3, 712–715.

Chischova E.A., Alzaydien A.S., 2009, The calculation of Rate Constants of Parallel-Consecutive Second Order Reaction, Australian Journal of Basic & Applied Sciences, 3, 3, 2828-2833.

Deng J.Z., Ge R.J., 2000, Calculation method, Xian: Xian Jiao tong University Press.

Erdoğdu F., Şahmurat F., 2007, Mathematical fundamentals to determine the kinetic constants of first-order consecutive reaction, Journal of Food Process Engineering, 30, 30, 407-420, doi: http://dx.doi.org/10.1111/j.1745-4530.2007.00116.x

Gábor L., 2015, Analytical solutions for the rate equations of irreversible two-step consecutive processes with second order later steps, J Math Chem, 53, 1759–1771, doi: 10.1007/s10910-015-0517-3.

Gagliano A., Nocera F., Patania F., Bruno M., Scirè S., 2016, Kinetic of the Pyrolysis Process of Peach and Apricot Pits by TGA and DTGA Analysis. International Journal of Heat and Technology, 34, S2, S553-S560. DOI: 10.18280/ijht.34S250

Ge H.C., Zhu M.L., 2013, An efficient method for solving reaction orders with Excel software, Laboratory science 16(01), 108-110, doi: 10.3969/j.issn.1672-4305.2013.01.033

He G.Y., 2001, Visual Basic Common Algorithms Assembly, Xian: Xidian University Press.

Hernández A., Ruiz M.T., 1998, An Excel template for calculation of enzyme kinetic parameters by non-linear regression, Bioinformatics, 14, 2, 227-228, doi: 10.1093/bioinformatics/14.2.227

Huang X.Z., Ji E.Y., 2012, Calculation of Chemical Reaction Constant and Reaction Order by Computer, Journal of Yantai University, 25, 3, 232-234, doi: 10.3969/j.issn.1004-8820.2012.03.016.

Li H.L., Zhang J.L., 2006, Study of calculating reaction stages by integral method using language C++, Computers and Applied Chemistry, 23, 11, 1117-1120, doi:10.3969/j.issn.1001-4160.2006.11.021

Li K.Q., 2011, A New Method for Obtaining Rate Constants of Consecutive First-order Reaction, Experiment Science & Technology, 09, 6, 22-23, doi: 10.3969/j.issn.1672-4550.2011.06.008

Mcmillan W.G., 2002, Determination of the Rate Constant Ratio in Competitive Consecutive Second-order Reactions, Journal of the American Chemical Society, 79, 18, 4838-4839, doi: 10.1021/ja01575a005

Mucientes A.E., 2009, Kinetic Analysis of Parallel-Consecutive First-Order Reactions with a Reversible Step: Concentration–Time Integrals Method, Journal of Chemical Education, 86, 3, 390-392, doi: 10.1021/ed086p390

Pan B.J., 2001, Application of Language C in Calculation of Reaction Stages by Differential Method, Computers and Applied Chemistry, 18, 2, 179-183, doi: 10.3969/j.issn.1001-4160.2001.02.012

Pedrazzi S., Allesina G.,Tartarini P., 2012, A KINETIC MODEL FOR A STRATIFIED DOWNDRAFT GASIFIER. International Journal of Heat and Technology, 30, 1, 41-44. DOI: 10.18280/ijht.300106

Seoud A.L.A., Abdallah L.A.M., 2010, Two optimization methods to determine the rate constants of a complex chemical reaction using FORTRAN and MATLAB, American Journal of Applied Sciences, 7, 4, doi: 10.3844/ajassp.2010.509.517

Ser P.B., Jun P.T., 2015, Chemical Kinetics of Consecutive and Parallel Reactions Both with a Reversible First Step, Bulletin of the Korean Chemical Society, 36, 9, 2221-2223, doi: 10.1002/bkcs.10428

Shi Y., 2008, Hierarchical differential evolution for parameter estimation in chemical kinetics. PRICAI 2008: Trends in Artificial Intelligence. Springer Berlin Heidelberg, doi: 10.1007/978-3-540-89197-0_81

Singer A.B., Taylor J.W., Barton P.I., Green W.H., 2006, Global Dynamic Optimization for Parameter Estimation in Chemical Kinetics, J. Phys. Chem. A, 110, 971-976. doi: 10.1021/jp0548873.

Su Z., 2005, A ratio of concentration and time method for determining a reaction order and calculation the rate constant, Computers & Applied Chemistry, 22, 3, 235-238, doi: 10.3969/j.issn.1001-4160.2005.03.017.

Xia S., Tang W.G., 2009, Application of Origin and Software MATLAB in the Solution to Chemical Reaction Order. Journal of Xihua University, 28, 4, 76-79. doi: 10.3969/j.issn.1673-159X.2009.04.020

Yao J.T., Wang A.H., 2005, The Kinetics of Consecutive Second-order Reaction by Computer Simulating Method, Journal of Zhengzhou University, 37, 2, 85-87, doi: 10.3969/j.issn.1671-6841.2005.02.023.

Zhong W., Tian Z., 2011, Numerical simulation for some kinds of complex chemical reaction kinetics, Chemical Engineering (China), 39, 8, 82-85, doi: 10.3969/j.issn.1005-9954.2011.08.020.