Determination of Heterogamous and Homogenous Reaction Rate Constants Using Non-linear Optimization.

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Abstract

Experimental reaction data must be fitted into a useful reaction rate equation in order to use in the simulation of reactor design and sizing. While optimization techniques of experimental data of homogenous reaction are well established, many challenges are encountered when experimental data are of catalytic reactions. A computer simulation tool has been developed to accept experimental reaction data and fit the data into a nonlinear reaction rate equation. More than 180 of the L-H reaction rate equations are built into the program. The program will estimate catalytic adsorption constants and other reaction rate constants, and recommend the best reaction rate equation. The non-linear optimization methods available in GAMS are used via a Visual Basic user-friendly interface.

Introduction

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. (Yang and Hougen, 1950) The algorithm for collecting information for catalytic reactor design is shown in Figure 1. The objective of the

research is to develop a computer optimization tool to determine the best catalytic and non-catalytic reaction rate equation and reaction rate constants based on available experimental data.
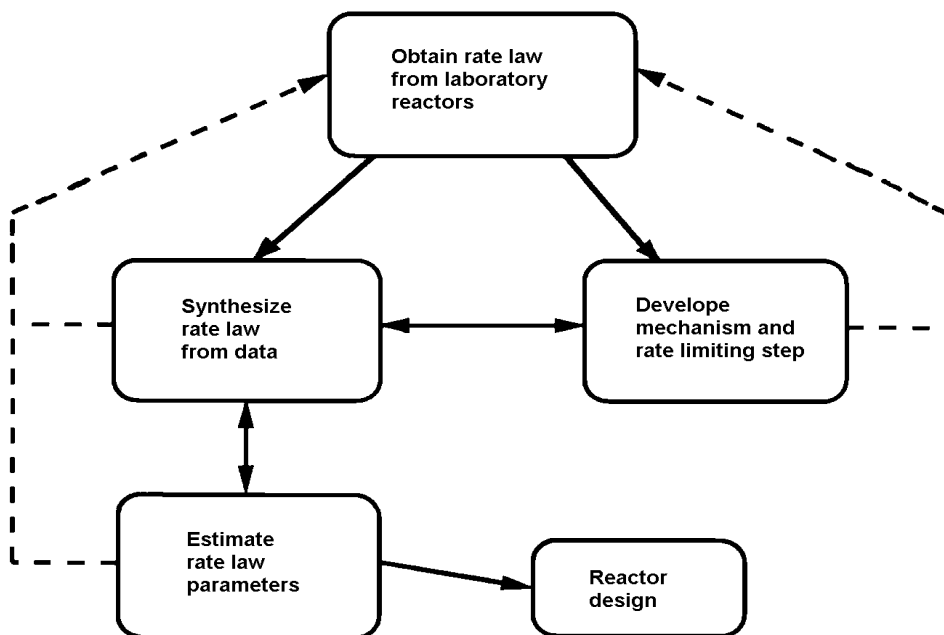

Figure 1. Collecting Information for Catalytic Reactor Design

Source: Fogler, H. Scott. (1994). Elements of Chemical Reaction Engineering (2nd ed.). Englewood Cliffs, NJ: Prentice Hall.

Experimental data of a homogeneous or heterogeneous reaction may be fitted into a theoretical, semi-theoretical, or empirical rate equation. The rate equation is used to predict the reaction rate within the ranges of the variables studied and in some cases to allow cautious extrapolation. This is most frequently done with a set of Langmuir-Hinshelwood (L-H) rate equations. The L-H rate equation of heterogeneous catalysis is widely used by chemical engineers in the correlation of experimental catalytic reaction rate data. (Kabel and Johanson, 1962) L-H rate equations are used to represent heterogeneous reactions where adsorption effects are important. With the knowledge of kinetic constants these rate equations are screened to reject those that are inadequate in the light of the data. (Kittrell, Hunter and Watson, 1965)

The optimization problem can be quite difficult for L-H rate equations because of many factors. First, these rate equations are frequently nonlinear with respect to the rate constants within these rate equations. Second, the number of rate constants contained in each rate equation

can be too many for the range of the experimental data. (Mezaki and Kittrell, 1967) Rate constants in L-H rate equation are optimized using the principle of minimization of sum of squares of residuals.

The present work can be used to find out possible rate equations for homogeneous and heterogeneous reactions. After testing corresponding rate equations versus available experimental data, the most suitable mechanism representing the reaction and the corresponding rate equation and constants can be selected on the basis of sum squares of residuals and sign of kinetic constant. NLP solver of GAMS is used to optimize the rate constants in Langmuir-Hinshelwood equations. NLP solver is used to minimize the sum of square of residuals.

Literature Survey

<u>Heterogeneous Reactions</u>

Langmuir-Hinshelwood rate equations have provided a pragmatic approach to the correlation of experimental data for heterogeneous catalytic reactions. Hougen and Watson

pioneered in this approach and showed the significant features of the method. (Lapidus and Peterson, 1965)

Hougen and Watson (1959) studied the case of vapor phase catalytic hydrogenation of mixed iso-octenes. Mixed iso-octenes are commercially known as codimer. The reaction is as follows.

$$C_8H_{16(g)} + H_{2(g)} \longleftrightarrow C_8H_{18(g)}$$
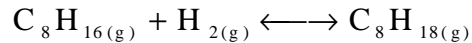
Hougen and Watson suggested 18 different mechanisms were possible and the final equation they suggested was:

$$r = \frac{kK_BK_Ap_Bp_A}{\left(1 + K_Ap_A + K_Bp_B + K_Rp_R\right)^2}$$

Where, A refers to hydrogen, B to unsaturated component, R to saturated component.

This is the classic case later studied by many more kinetists using different mathematical methods to estimate the rate constants.

Yang and Hougen (1950) have described mathematical expression for heterogeneous rate equation as combination of three terms, the kinetic term, the potential term, and the adsorption term, arranged thus

$$r = \frac{(kinetic\ \ term)(potential\ \ term)}{(adsorption\ \ term)^N}$$

Langmuir-Hinshelwood Approach

The approach in determining catalytic and heterogeneous mechanisms is usually termed as the Langmuir-Hinshelwood approach. It was derived from ideas proposed by Hinshelwood based on Langmuir's principles for adsorption. It is based on the following hypotheses:

1. Uniformly energetic adsorption sites.
2. Monolayer coverage.
3. No interaction between adsorbed molecules. (Froment and Bischoff, 1979)

Once the reactant has been adsorbed onto the surface, it is capable of reacting in number of ways to form the reaction product. Three of these ways are:

1. Single site mechanism
2. Similar or dissimilar dual site mechanism
3. Eley-Rideal Mechanism

Algorithm for Rate Constant Optimization

There are broadly two types of estimation procedures, namely linear least square method and nonlinear least square method. The objective of both methods is to arrive at the most probable or "best" relationship, which will represent all of the experimental data with minimum average error or deviation.

Linear Least Square Method

The method of linear least squares may be used to determine the best constants in a given form of equation and also for establishing the best form of equation for a given set of data. The best constants are first evaluated for each form of equation under consideration. The best form of equation is then that for which the average of the squares of the deviations is the least. (Hougen and Watson, 1959)

Unfortunately this method has a number of defects. (Seinfeld and Lapidus, 1974) Foremost among these is the fact that few rate equations of any complexity occur in the desired linear form. As a result the rate equation must be linearized or rearranged to be handled by this method. Thus the original distribution of errors are not preserved.

Nonlinear Least Squares Method

In a broad-gauged description of this method, one attempts to minimize sum of squares of residuals, SSR, in an iterative fashion rather than in a single step.

Difficulties faced on linear least square method are eliminated in nonlinear least square method. The algebraic rate equation is used in the original form without imposing arbitrary transformations. Thus the minimization of the sum of squares of the errors is appropriate in terms of untransformed variables.

The nonlinear least square method has been extensively used to solve the problem of rate constant optimization in heterogeneous catalytic reaction rate equation.

Application of GAMS for Rate Constant Optimization

Langmuir-Hinshelwood catalytic rate equations are essentially nonlinear. GAMS (General Algebraic Modeling System; GAMS Release 2.25 © GAMS Development Corporation) is used for formulating, solving, and analyzing optimization problems. The design of GAMS has incorporated ideas drawn from relational database theory and mathematical programming. (Brooke, Kendrick 1997) GAMS provides a solver called NLP to solve nonlinear programming problems. NLP solver can be used to minimize the sum of squares of residuals. Lower bounds of rate constants to be estimated are needed to initialize the program. NLP solver in GAMS returns the optimized rate constants if the lower bounds are lower than optimum value. GAMS also returns the sum of squares of residuals along with the optimized rate constants.

Criterion for Rate equation Selection

It is the requirement of the theory upon which L-H equations are based that all rate constants must have positive or zero values. (Hougen and Watson, 1959) Rate constants actually are adsorption equilibrium constants. Adsorption equilibrium constant can either be positive or zero that is no adsorption is taking place. But it cannot be negative. All the rate equations are rejected which give negative rate constants. The rate equation with all positive rate constants and with lowest sum of squares of residuals is considered as the suitable rate equation.

GAMS has facility to enter lower bounds for rate constants. So the rate constant will never take the negative value even if the rate equation is not suitable. To solve this problem one can try different lower bounds. For the best fitting rate equation all lower bounds will converge to the same values of rate constants, while for unsuitable rate equations the final values of rate constants will be different. After selecting the rate equations with positive rate constants one can compare the sum of squares of residuals to select the best rate equation.

<u>Optimization of Kinetic Constant for Homogeneous Reactions</u>

The principle of minimization of sum of squares of residuals is used for optimization of kinetic constants in homogeneous reactions (Himmelblau, Jones and Bischoff, 1967). The program is having a subroutine to optimize kinetic constants in homogeneous reactions. The necessary data is number of reactions, number of components, stoichiometry of reactions and guess values of forward and backward reaction constants along with experimental data of concentration and time. The program can produce tabular and graphical output along with optimized rate constants.

Program Features

The program developed in this study is a useful tool in determining the kinetic rate equation and optimizing the rate constants of homogeneous and heterogeneous reactions. The interface is user friendly and very easy to understand.

<div align="center">Heterogeneous Catalytic Reactions</div>

Heterogeneous catalytic reactions can be divided into four basic reactions. Each reaction could be reversible or irreversible. The program displays various L-H equations for each reaction type, depending upon whether the reaction is reversible or irreversible. L-H equation is determined by species that are adsorbed and rate controlling reaction step. Combinations of adsorbed species and rate controlling steps are given on "Mechanism" tab (see Figure 2).

Table 1 gives the number of mechanisms available for each reaction including reversible and irreversible reactions.

Table 1.

Number of Mechanisms Available for Each Reaction

Type of Reaction	Number of Mechanisms Available
$A \longleftrightarrow R$	24
$A \longleftrightarrow R + S$	36
$A + B \longleftrightarrow R$	54
$A + B \longleftrightarrow R + S$	74

Lower bounds of rate constants are entered as starting point for GAMS. If lower bounds of rate constants remain unchanged in GAMS, then still lower values of rate constants need to be entered. This way one can optimize the rate constants. Lowest values one can enter are zero.

Determination of Mechanism

File   Data Type

| Reactions | Mechanism | Experimental Data | Result |

A, B, R adsd
○ Adsorption of A   ○ Adsorption of B
◉ Surface Reaction
○ Desorption of R

A not adsd, B, R adsd
○ Adsorption of B
○ Surface Reaction
○ Desorption of R

A not adsd, B adsd, R not adsd
○ Adsorption of B
○ Surface Reaction

A, B adsd, R not adsorbed
○ Adsorption of A
○ Adsorption of B
○ Surface Reaction

A adsd, B not adsd, R adsd
○ Adsorption of A
○ Surface Reaction
○ Desorption of R

A adsd w/ disso., B, R adsd
○ Adsorption of A   ○ Adsorption of B
○ Surface Reaction
○ Desorption of R

A adsd w/ disso., B not, R adsd
○ Adsorption of A
○ Surface Reaction
○ Desorption of R

A adsd w/ disso., B adsd, R not adsd
○ Adsorption of A
○ Adsorption of B
○ Surface Reaction

A adsd w/ disso., B, R not adsd
○ Adsorption of A
○ Surface Reaction

$$r = \frac{k \; K_A K_B \, p_A p_B}{\left(1 \; +K_A p_A \; +K_B p_B \; +K_R p_R \right)^2}$$
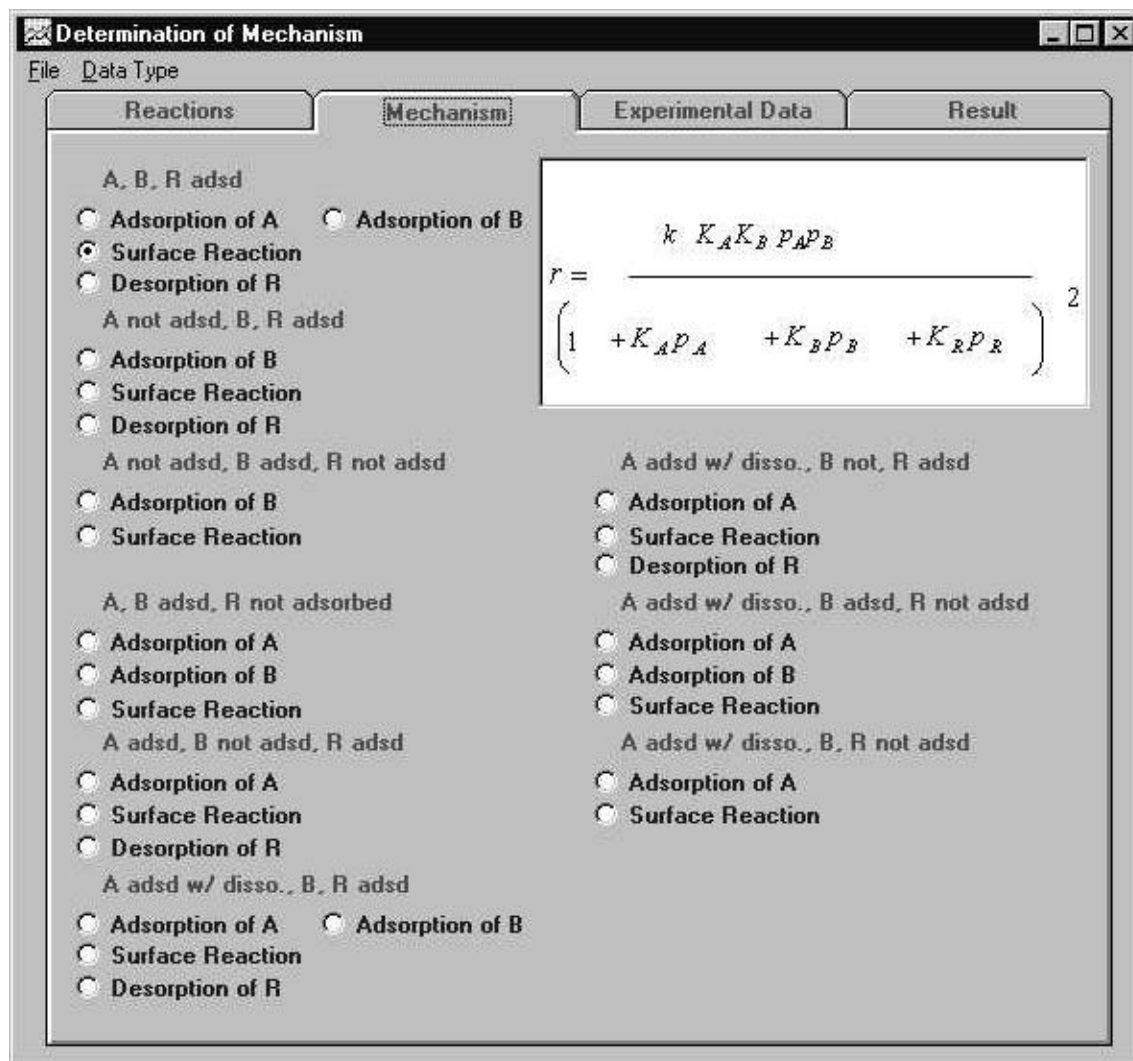
Figure 2. Heterogeneous Reactions: Mechanism Tab

The rate constants are changed in such a way that calculated data is as close to the experimental data as possible. When the difference between calculated data and experimental data is the minimum then rate constants are optimized. Usually the equation, which gives the minimum sum of squares of residuals and all positive rate constants, is the suitable one.

The result tab displays the sum of squares of residuals and optimized rate constants along with the rate equation. If the result is not satisfactory then user can select other mechanism or he can enter new guessed rate constants and run the program again.

<center>Homogeneous Catalytic Reactions</center>

Homogeneous catalytic reactions are those reactions in which a catalyst is in solution with at least one of the reactants. An example of homogeneous catalysis is the industrial Oxo process for manufacturing normal isobutylaldehyde. There are three basic types of homogeneous reactions: series, parallel and independent. (Fogler, 1994)

In parallel reactions (also called competing reactions) the reactant is consumed by two different reactions to form different products. For example, $\begin{array}{l} A \xrightarrow{\;k_1\;} B \\ A \xrightarrow{\;k_2\;} C \end{array}$

In series reactions, also called consecutive reactions, the reactant forms an independent product, which reacts further to form another product. For example, $A \xrightarrow{\;k_1\;} B \xrightarrow{\;k_2\;} C$

Homogeneous reactions involve a combination of both series and parallel reactions, such as $\begin{array}{l} A + B \longrightarrow C + D \\ A + C \longrightarrow E \end{array}$

Complex Reactions:

A system of complex chemical reaction in which there is coupling between all species is shown in Figure 3. There are three chemical species, A_1, A_2, and A_3, where these symbols stand for the species as well as concentration and they are connected by reaction scheme (Amundson, 1966)
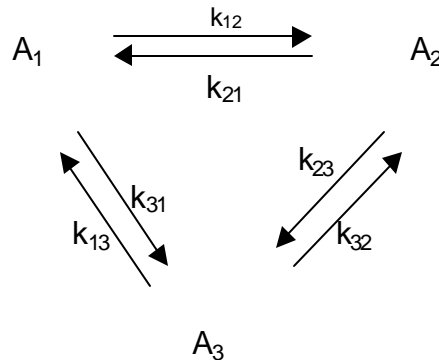
<center>Figure 3. System of Complex Reaction</center>

Source: Amundson, N.R. (1966). Mathematical Methods in Chemical Engineering. Englewood Cliffs, New Jersey: Prentice Hall

Where, k_{ij} is the absolute rate constant and $k_{ij}A_j$ is the rate of formation of A_i from A_j in moles per unit volume per unit of time. For the above reaction scheme, the rate equations are

$$\frac{dA_1}{dt} = -(k_{12} + k_{31})A_1 + k_{21}A_2 + k_{31}A_3$$

$$\frac{dA_2}{dt} = k_{21}A_1 - (k_{12} + k_{32})A_2 + k_{23}A_3$$

$$\frac{dA_3}{dt} = k_{31}A_1 + k_{32}A_2 - (k_{13} + k_{31})A_3$$

Such system may be generalized to n chemical species, each of which is coupled to every other species by chemical reaction to give ($k_{jj} = 0$ for all j)

$$\frac{dA_1}{dt} = -\sum_{j=1}^{n} k_{1j}A_1 + k_{21}A_2 + k_{31}A_3 + \cdots + k_{n1}A_n$$

$$\frac{dA_2}{dt} = k_{21}A_1 - \sum_{j=1}^{n} k_{2j}A_2 + k_{23}A_3 + \cdots + k_{n2}A_n$$

$$\vdots$$

$$\frac{dA_n}{dt} = k_{n1}A_1 + k_{n2}A_2 + \cdots + k_{n,n-1}A_{n-1} - \sum_{j=1}^{n} k_{nj}A_n$$

This system of equations is solved using nonlinear least square method to obtain unknown k_{ij}, provided concentration-time data is given.

Case Study

Various cases were selected from the literature, and solved using the NLP solver in GAMS.

The vapor phase hydrogenation reaction of mixed iso-octenes to the corresponding iso-octanes (Hougen and Watson, 1959) is:

$$C_8H_{16}(g) + H_2(g) \longleftrightarrow C_8H_{18}(g)$$
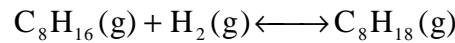
Authors suggested reaction between molecularly adsorbed hydrogen and adsorbed codimer with surface reaction controlling mechanism be the most suitable for given experimental data. The equation is:

$$r = \frac{kK_A K_B P_A P_B}{\left(1 + K_A P_A + K_B P_B + K_R P_R\right)^2}$$

Results from literature and REACAT are given in from Table 2 to Table 4.
k in gmol/(g catalyst hr), K_A, K_B, K_R in atm^{-1}.

Table 2

Result obtained by Hougen and Watson (1959) (Linear least square method)

Rate Constant	200°C	275°C	325°C
k	0.644	0.830	0.954
K_A	0.383	0.246	0.190
K_B	0.580	0.503	0.469
K_R	0.489	0.0646	0.0222
SSR	7.315E-5	2.427E-4	1.347E-4

Table 3

Result obtained by Blakemore and Hoerl (1963) (Nonlinear least square method)

Rate Constant	200°C	275°C	325°C
k	0.65	0.94	0.99
K_A	0.38	0.24	0.18
K_B	0.55	0.58	0.40
K_R	0.54	0.23	1E-5
SSR	1.1E-5	1.4E-5	1.4E-5

Table 4

Result using REACAT (GAMS)

Rate Constant	200°C	275°C	325°C
k	0.709964	1.036669	0.890046
K_A	0.331107	0.220122	0.188581
K_B	0.481635	0.587166	0.413597
K_R	0.417908	0.341022	0
SSR	6.239E-5	8.064E-5	3.433E-5

GAMS program predicted zero value for K_R because GAMS provides syntax to enter the lower bound of a rate constant. Result obtained from REACAT for rate constant k, K_B and K_A varies ±10% from result given by Blakemore and Hoerl. Rate constant K_R varies more widely from 22% for 200°C to 48% for 275°C. For 325°C, Blakemore and Hoerl calculated value of K_R

as 1E-5, which is almost zero. The result for 200°C, which contains optimized rate constants, sum of squares of residuals (SSR) and rate equation is shown in Figure 4.
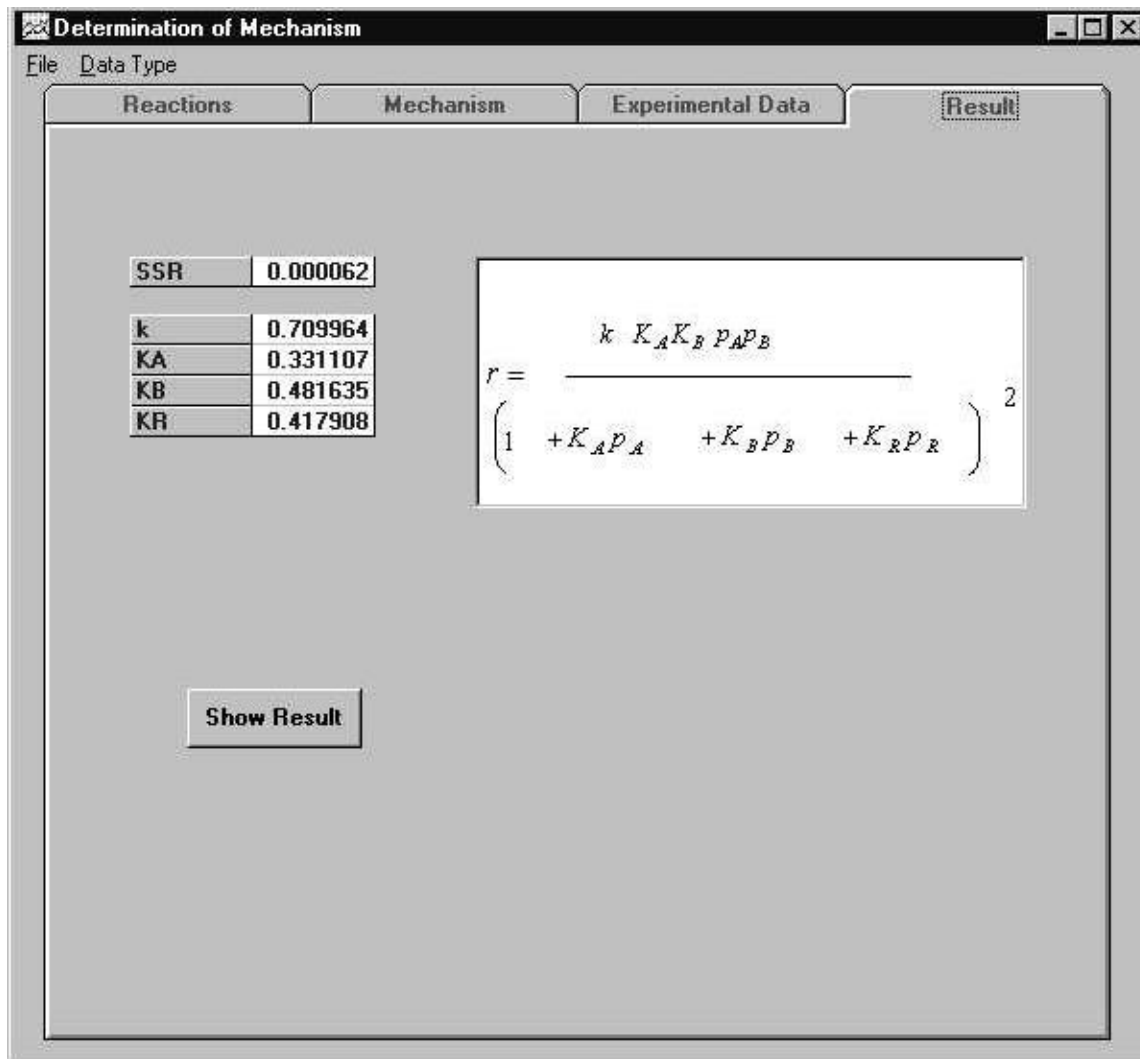

Figure 4. Result Tab

Conclusion

A program for the optimization of kinetic rate constants for homogeneous and heterogeneous reactions was developed in this work. The NLP solver of GAMS was used for optimization of rate constants in heterogeneous reactions. Visual Basic 5 was used as visual interface for input and output. The study covered various types of mechanisms and rate controlling steps in heterogeneous reactions. The total number of L-H rate equations included for all four types of reactions and for reversible-irreversible reactions is 188. Also simple and complex homogeneous reactions were studied to optimize the rate constants.

The results generated by the program include the sum of squares of residuals and the values of kinetic constants. In case of homogeneous reactions, the graph of concentration as function of time is displayed. These results can be stored in data files and further used for reactor design. It is possible to change the guess values of kinetic constants and see the effect on sum of squares of residuals. Also it is possible to check the fit of experimental data into various mechanisms and rate controlling steps.

GAMS proved to be a powerful tool to solve the optimization problem in heterogeneous catalysis. NLP solver in GAMS converges the program even if initial guesses are far away from global optimum.

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