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# QUANTITATIVE MODELLING OF CHEMICAL REACTIONS

## 1. QUANTITATIVE APPROACH TO INVESTIGATING COMPLEX CHEMICAL REACTIONS. A CONVERSION MODEL OF REACTION

A review of literature has revealed that the majority of experimental investigations of organic chemistry are the so-called classical ones. These works, forming today a practical basis of most theoretical contributions to this field of research, as a rule, include the methods of determining the chemical structure and composition of organic reaction products. Besides, many publications report results of investigating the influence of different parameters on the yield of products, such as chemical nature of catalysts and medium, ratio of ingredients, reaction temperature and time, activating or inhibiting agents. Conclusions have been drawn mostly on the reactivity of components, chemism and possible routes of reactions, optimum conditions of obtaining the desired products.

Only some of the reactions studied are subjected to a quantitative study, involving usually reaction systems which proceed in no more than three predetermined directions. Most of the kinetic investigations with a view to elucidating the reaction mechanism and reactivity of organic compounds belongs here. Kinetic and other physicochemical methods are applied to investigations, while experimental data are often computer-processed to determine the kinetic constant values. Reactions which are the key of technological processes are also subjected to kinetic investigations, using preferably complex methods of experimental design and optimization [1, 2]. The latter, however, do not always provide quantitative information about the reactivity of compounds. On the other hand, an ever-increasing application of multidirectional reactions with polyfunctional compounds to organic synthesis [3] requires the development of simplified procedures for their quantitative modelling and optimization.

On the basis of experimental **data of the classical works** it can be concluded that their main drawback is the lack of material balances of components at the stages of conversion of ingredients under study. The authors often report data on the composition of initial reaction media and the yield of reaction products. However, usually no changes in the concentration of initial substances have been established, due to which the above-mentioned material balances of components in the course of reaction cannot be elucidated. This converts the quantitative results of investigation into **qualitative ones**, despite the accuracy of experimental design and determination of reaction product yields. As a result, the conclusions drawn in these works are also qualitative, possibly leading to contradictory and false conceptions about the reactivity and reaction mechanism of the compounds under study. Moreover, the application of the results of these investigations to synthetic research requires a number of additional quantitative studies, not always presenting the expected and reliable results.

The present study reports on some methodological principles, contributing to the removal of the drawbacks, and aims at providing **quantitative information** about complex organic reactions, using neither the complex computational methods of experimental design nor the kinetic and other labour-consuming methods. Such a quantitative experimental data

processing can be carried out by determining the concentration of all initial ($X$, $Y$) and formed compunds ($Z_i$) on at least three or more stages of the conversion of ingredients. Under the similar initial reaction conditions, the stages of the conversion of ingredients need not be strictly similar, but they should enable reliable interpolation or extrapolation of the experimental data.

If difficulties arise in establishing the chemical structure and composition of all the compounds formed, the concentrations of unknown products may be expressed by the total molecular content of their initial reagents. To obtain quantitative information about a complex reaction between two ingredients, in many cases it is expedient to perform four conversion experiments at constant temperature, varying the initial concentration and ratio of ingredients within a possibly wide range. The concentration range of ingredients, however, should allow the determination of changes in the concentration of components with admissible error. The following ratios of ingredients should meet these requirements:

$$[X]_0 : [Y]_0 = 3:3;\ 1:3;\ 3:1;\ 1:1.$$

The experimental data obtained about the changes in the absolute concentrations of components are then transformed into dimensionless values of relative concentrations, depending on the conversion of one initial substance expressed as a function of conversion of this ingredient. As a result of such processing, **graphic integral conversion models** of reactions are obtained:

$$\frac{y_{i0} - y_i}{x_0 - x},\ \frac{z_i}{x_0 - x} = \Phi_i\left(\frac{x_0 - x}{x_0}\right).$$

To obtain more information, analogous conversion models may also be constructed as graphic functions of either the degree of conversion of the other ingredient or a change in the concentration of major products:

$$\frac{x_{i0} - x_i}{y_0 - y},\ \frac{z_i}{y_0 - y} = \Phi_i\left(\frac{y_0 - y}{y_0}\right);$$

$$\frac{x_{i0} - x_i}{z_1},\ \frac{y_{i0} - y_i}{z_1},\ \frac{z_i}{z_1} = \Phi_i\left(\frac{z_i}{x_0}\right),$$

where $x_i$, $y_i$ — the concentrations of initial substances;
$z_i$ — the concentrations of the products obtained.

The dimensionless integral conversion models of reaction under comparison allow extrapolation of the ratios of decreasing components and those formed to the initial reaction conditions, enabling elucidation of parallel reactions of the system, as well as dependence of their relative rate on the concentration or ratio of ingredients. Also, components undergoing successive reactions may be elucidated and a qualitative dependence of the latter on the concentration of components in the reaction system established. Semiquantitative estimation of the relative rate of components conversion made on the basis of graphic dimensionless integral models which depend on the concentration and ratio of components, enable us to set up a system of **differential equations of conversion of components** described by the derivatives:

$$\frac{dy_i}{dx},\ \frac{dz_i}{dx} = F_{ij}(k_j,\ x,\ y_i,\ z_i),$$

where $k_j$ — the relative kinetic constants of reactions.

The above transformations have been successfully used by I. Ugi and G. Kaufhold in [4], and the author in [5] to calculate the partial kinetic constants of the complex cationic telomerization reactions of isoprene. A graphic integral modelling of the last reaction was performed much earlier [6].

If graphic integral models do not reveal all directions of conversion and dependences of reactions, some alternative systems of differential equations of components conversion may be formed. The alternative differential conversion models set up are checked for reliability by computer-aided approximation of the calculated values of components concentrations with experimental data, determining the reliable values of the relative kinetic constants, $k_j$, found by the method of least squares [7]. Such mathematical experimental data processing suggests carrying out additional experiments, changing the ratios and degrees of conversion of ingredients to obtain more reliable values of the constants searched for. For the relative kinetic constant values determined, the Arrhenius parameters may also be calculated, carrying out experiments at different temperatures. The differential conversion models of reaction constructed contribute to further optimization of the yield of the desired products depending on the ratio and degree of conversion of components, as well as the calculation of optimum temperature parameters of a process. Quantitative differential conversion models are also useful for further modelling of the kinetics of complex reactions to calculate absolute kinetic constant values.

**Example.** A catalytic reaction between compounds $X$ and $Y$ proceeding at the catalyst concentration of $[\text{Cat}] \cong 10^{-3}$ mole $\cdot$ $l^{-1}$ was investigated. Attempts to determine the reaction order failed as it changed due to the catalyst concentration, the initial concentration and degree of conversion of reactants. By chemical and physicochemical investigations it was established that the reaction affords three isomeric addition products: $X+Y \rightarrow Z_1$, $Z_2$, $Z_3$. Moreover, one initial component undergoes isomeriza-

**Determination of the composition of reaction products**

$$X+Y \xrightarrow{\text{Cat.}} Z_1,\ Z_2,\ Z_3;\quad X \xrightarrow{\text{Cat.}} Z_4$$

| | Concentration, mole $\cdot$ $l^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | $y$ | $x$ | $z_1$ | $z_2$ | $z_3$ | $z_4$ |
| Experiment 1 (b) | | | | | | |
| | 2.0 | 2.0 | — | — | — | — |
| | 1.60 | 1.48 | 0.26 | 0.12 | 0.02 | 0.12 |
| | 1.20 | 0.98 | 0.48 | 0.24 | 0.08 | 0.22 |
| | 0.80 | 0.49 | 0.62 | 0.36 | 0.22 | 0.31 |
| | 0.50 | 0.15 | 0.65 | 0.45 | 0.40 | 0.35 |
| Experiment 2 (a) | | | | | | |
| | 2.0 | 1.0 | — | — | — | — |
| | 1.80 | 0.77 | 0.14 | 0.06 | 0.01 | 0.03 |
| | 1.50 | 0.44 | 0.32 | 0.15 | 0.03 | 0.06 |
| | 1.30 | 0.22 | 0.43 | 0.21 | 0.06 | 0.08 |
| Experiment 3 (c) | | | | | | |
| | 1.0 | 2.0 | — | — | — | — |
| | 0.70 | 1.51 | 0.19 | 0.09 | 0.02 | 0.19 |
| | 0.40 | 1.00 | 0.31 | 0.18 | 0.11 | 0.40 |
| | 0.20 | 0.64 | 0.32 | 0.24 | 0.24 | 0.56 |
| Experiment 4 (d) | | | | | | |
| | 0.5 | 1.0 | — | — | — | — |
| | 0.30 | 0.68 | 0.12 | 0.06 | 0.02 | 0.12 |
| | 0.22 | 0.54 | 0.15 | 0.08 | 0.05 | 0.18 |
| | 0.15 | 0.39 | 0.16 | 0.11 | 0.08 | 0.26 |
| | 0.07 | 0.26 | 0.15 | 0.13 | 0.15 | 0.31 |

tion to yield an isomer $X \rightarrow Z_4$. Analytical methods have been developed to determine the concentration of initial compounds and those obtained in reaction media with reliable error of $\pm$—0.005 mole $\cdot$ $l^{-1}$.

The catalyst concentration had no significant influence upon the composition of reaction products, but it affected only the reaction rate. It was established that the latter does not depend proportionally on the catalyst concentration. For modelling the reactions conversion experiments were carried out (the Table). The results of processing experimental data into dimensionless concentrations of components are shown in Fig. 1.

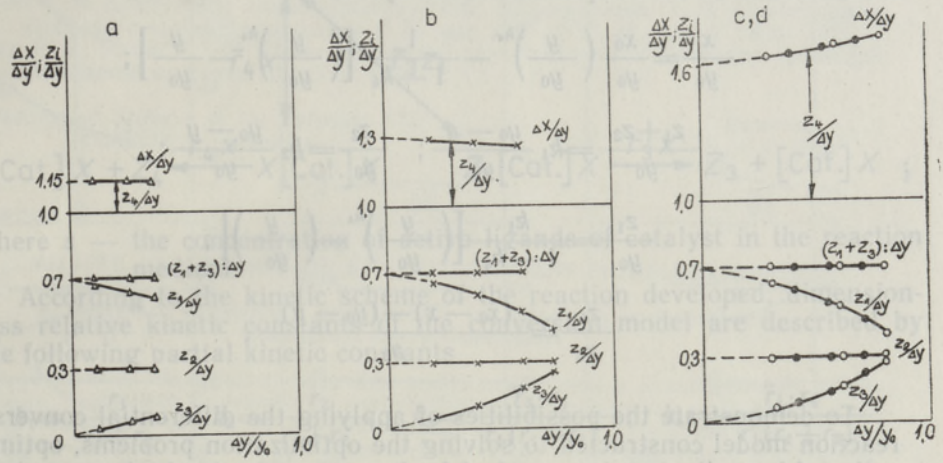



Fig. 1. Integral graphic conversion model of the reaction $X+Y \longrightarrow Z_1$, $Z_2$, $Z_3$; $X \longrightarrow Z_4$.
△ $x_0 : y_0 = 1:2$ [mole $\cdot$ $l^{-1}$] (a); × $x_0 : y_0 = 2:2$ [mole $\cdot$ $l^{-1}$] (b); ○ $x_0 : y_0 = 2:1$ [mole $\cdot$ $l^{-1}$] (c); ● $x_0 : y_0 = 1:0.5$ [mole $\cdot$ $l^{-1}$] (d).
$\Delta x = x_0 - x$; $\Delta y = y_0 - y$.

By the extrapolation of the changes in the dimensionless concentrations of components to the initial reaction conditions, it is established that the adducts $Z_1$ and $Z_2$ are derived from $Y$ at a ratio of 0.7:0.3, respectively. Adduct $Z_3$ results from the isomerization of $Z_1$, while the absolute concentrations and the ratio of $x:y$ do not influence the relative rate of formation of the adducts. The relative rate of isomerization $Z_1 \rightarrow Z_3$ depends only on the $z_1:y$ ratio and increases with its increase. The relative rate of isomerization $X \rightarrow Z_4$ does not depend on the absolute values of $x$ and $y$ and is directly proportional to the quotient of $x:y$ (at the $x_0:y_0$ ratio of 1:1, $z_4:\Delta y = 0.3$). An increase in the rate of isomerization of $X$ at a high degree of conversion of $Y$ in excess, $X$ is accounted for the corresponding changes in the $x:y$ ratio. On the basis of the integral regularities established for a given reaction a system of differential equations of components conversion may be set up relative to the ingredient $Y$, including the following kinetic terms:

$$\frac{dx}{dy} = 1 + k_4 \frac{x}{y}; \qquad \frac{dz_4}{dy} = -k_4 \frac{x}{y}; \tag{1}$$

$$\frac{dz_1}{dy} = -k_1 + k_3 \frac{z_1}{y}; \quad \frac{dz_2}{dy} = -k_2;$$

$$\frac{dz_3}{dy} = -k_3 \frac{z_1}{y},$$

where $x$, $y$, $z$ — the concentrations of the corresponding components;
$k_j$ — the relative kinetic constants.

By computer-aided integration of the differential kinetic equations of conversion formulated approximating the calculated data with experimental ones (the Table) by using the method of least squares [7], the following numerical values of the constants searched for have been determined:

$$k_1=0.7;\ k_2=0.3;\ k_3=0.6;\ k_4=0.3. \tag{2}$$

It should be pointed out that a solution of this differential conversion reaction model is analytical and integral according to a change in the concentration of all components of the system:

$$\frac{x}{y_0}=\frac{x_0}{y_0}\left(\frac{y}{y_0}\right)^{k_4}-\frac{1}{1-k_4}\left[\left(\frac{y}{y_0}\right)^{k_4}-\frac{y}{y_0}\right];$$

$$\frac{z_1+z_2}{y_0}=k_1\frac{y_0-y}{y_0};\quad \frac{z_2}{y_0}=k_2\frac{y_0-y}{y_0};$$

$$\frac{z_1}{y_0}=\frac{k_1}{1-k_4}\left[\left(\frac{y}{y_0}\right)^{k_4}-\left(\frac{y}{y_0}\right)\right];$$

$$\frac{z_4}{y_0}=\frac{(x_0-x)-(y_0-y)}{y_0}.$$

To demonstrate the possibilities of applying the differential conversion reaction model constructed to solving the optimization problems, optimum ratios of ingredients were searched for by a computer to obtain a maximum yield $\frac{z_1+z_2}{y_0}$ on the initial condition that the content of the isomer $Z_3$ in the adduct should not exceed $\frac{z_3}{z_1+z_2}\leqslant 0.1$ and $x/y_0\leqslant 0.01$. As a result of optimization the following ratios of components were established:

$x_0:y_0=0.3:1.0$; the residual quantity of $x/y_0$ 0.006 at a degree of conversion of $y/y_0=0.28$;

the calculated ratios of isomers in the product $z_1:z_2:z_3=0.63:0.30:0.07$;

the desired product yield $\frac{z_4+z_2}{100x_0}=86.8\%$ of theoretical.

To find the possibilities of transforming conversion equations of reaction into kinetic ones, we can use an expression of the change in initial compound concentration described through the derivative of the concentration of initial reactants in time and taken as a conversion model attribute:

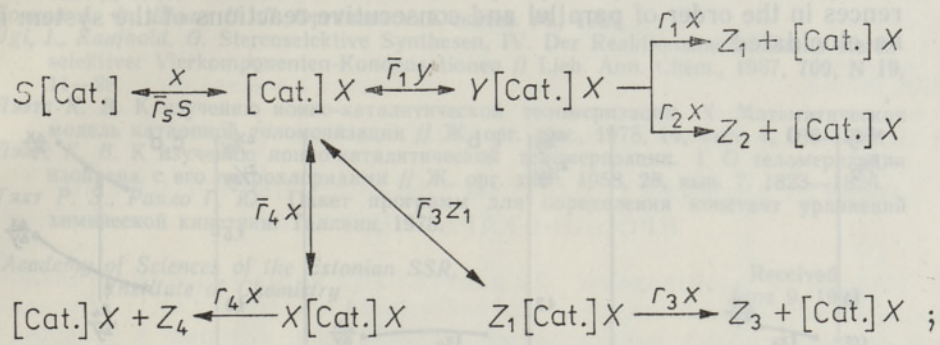
$$\frac{dy}{dt}=-\frac{x\cdot y}{F_t([\text{Cat.}],\ k_t,\ x,\ y,\ z_1,\ s)}, \tag{3}$$

where $F_t$ — a function of the dependence of reaction time on the concentration of intermediate reaction complexes of a catalyst with ingredients $(x,\ y,\ z_1)$, as well as with the active ligands and other various factors of the reaction medium $(s_i)$ described by partial kinetic constants $k_j$. The kinetic equations of the components are expressed as follows:

$$\frac{dx}{dt}=-(xy+k_4x^2):F_t,\quad \frac{dz_1}{dt}=(k_1xy-k_3z_1x):F_t,$$

$$\frac{dz_3}{dt}=k_3z_1x:F_t,\quad \frac{dz_2}{dt}=k_2xy:F_t,\quad \frac{dz_4}{dt}=k_4x^2:F_t. \tag{4}$$

Proceeding from the theoretical ideas on the intermediate activated reaction complexes, on the basis of the total kinetic equations formulated and the experimental data presented in the example, the kinetic scheme of the reaction may be expressed as follows




where $s$ — the concentration of active ligands of catalyst in the reaction medium.

According to the kinetic scheme of the reaction developed, dimensionless relative kinetic constants of the conversion model are described by the following partial kinetic constants

$$k_1=\frac{r_1}{r_1+r_2},\quad k_2=\frac{r_2}{r_1+r_2},\quad k_3=\frac{\bar{r}_3\cdot r_3}{\bar{r}_1(r_1+r_2)},\quad k_4=\frac{\bar{r}_4\cdot r_4}{\bar{r}_1(r_1+r_2)}.$$

On the basis of the kinetic scheme proposed for a given reaction, kinetic equation may be written as

$$\frac{dy}{dt}=-\frac{xy}{F_t}=-\frac{[\text{Cat.}]\bar{r}_1(r_1+r_2)x\cdot y}{\frac{\bar{r}_s s}{x}+1+\bar{r}_1 y+\bar{r}_3 z_1+\bar{r}_4 x}. \tag{5}$$

The reaction rate equation formed includes, in addition to the relative kinetic constants, also 5 partial one- and two-dimensional kinetic constants whose determination is an additional problem. However, the values of the mentioned partial kinetic constants do not influence those of relative kinetic constants which may be previously calculated with high reliability, using the conversion reaction model proposed.

To sum it up, cases where parallel and consecutive reactions are not of the same order as the main reaction should be discussed. From the kinetic model of the reaction it is apparent that all irreversible reactions involved are of the second order. If we assume that the isomerization reactions are not of the second, but the first order, i. e.

$$\frac{dz_3}{dt}=k_3 z_1 : F_t,\quad \frac{dz_4}{dt}=k_4 x : F_t,$$

then the conversion equations of kinetics are transformed, including besides dimensionless kinetic terms also one-dimensional members:

$$\frac{dx}{dy}=1+\frac{0.3}{y},\quad \frac{dz_1}{dy}=-0.7+0.6\frac{z_1}{xy}. \tag{6}$$

The new conversion equations of the reaction (6) were subjected to computer-aided integration, using the initial concentrations $x_0$ and $y_0$, stages of conversion $\Delta y$ (the Table) and the relative kinetic constants determined (2).

The calculated integral conversion models of reaction obtained are shown in Fig. 2. A comparison of the kinetic curves shows that the relative rate of conversion of components, whose kinetic equations comprise one-dimensional members, depends on the initial absolute concentration values of ingredients. Consequently, by means of conversion models, also differences in the order of parallel and consecutive reactions of the system may be elucidated.

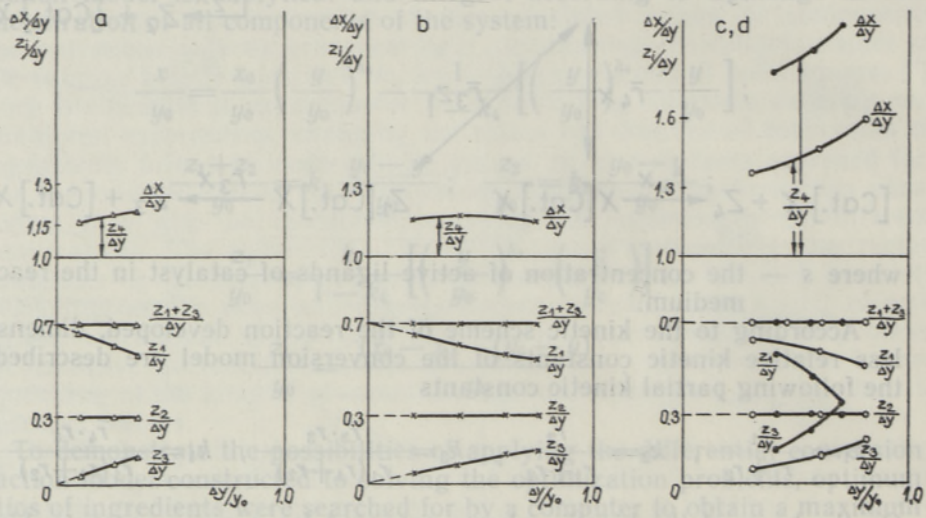



Fig. 2. Conversion model of the reaction

$X+Y \xrightarrow{0.3\,k} Z_1 \xrightarrow{0.6\,k} Z_3$; $X+Y \xrightarrow{0.3\,k} Z_2$; $X \xrightarrow{0.3\,k} Z_4$.

△ $x_0 : y_0 = 1 : 2$ [mole · l$^{-1}$] (a); × $x_0 : y_0 = 2 : 2$ [mole · l$^{-1}$] (b); ○ $x_0 : y_0 = 2 : 1$ [mole · l$^{-1}$] (c); ● $x_0 : y_0 = 1.0 : 1.5$ [mole · l$^{-1}$] (d).

$\Delta x = x_0 - x$; $\Delta y = y_0 - y$.

In conclusion we can say that a new simplified experimental and computational approach to quantitative modelling of complex reaction systems of organic compounds, involving parallel and successive reactions, has been suggested.

The procedure consists in the experimental determination of a change in the material balances of reactants, depending on the ratio and degree of conversion of components. For quantitative processing, experimental data are transformed into dimensionless integral graphic models of components conversion, on the basis of which differential conversion equations of a reaction are set up: $dx_i/dx = F_{ij}(k_j, x_i)$ ($x_i$ — the concentrations of components, $k_j$ — the relative kinetic constants). The numerical values of the constants $k_j$ are determined by computer-aided approximation of experimental data.

Methods of constructing conversion models and determining the values of relative kinetic constants have been considered on an example of a complex catalytic reaction. Possibilities of applying the conversion model to optimizing the composition and the yield of desired products with a view to formulating complete kinetic schemes and equations of the reaction have been demonstrated. The new methodological principles worked out contribute to obtaining quantitative information about complex organic reactions.

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## KEEMILISTE REAKTSIOONIDE KVANTITATIIVSEST MODELLEERIMISEST

### 1. Keeruliste orgaaniliste reaktsioonide kvantitatiivne uurimismeetod. Reaktsiooni konversioonimudel


On esitatud uus lähenemisviis keeruliste reaktsioonisüsteemide kvantitatiivseks modelleerimiseks. See seisneb komponentide materjalibilansside määramises reaktsiooni käigus olenevalt lähteainete suhtest ja konversiooniastmest. Saadud katseandmed viiakse üle graafilisteks integraalseteks konversioonimudeliteks, mille alusel koostatakse reaktsioonile diferentsiaalkonversioonivõrrandite süsteem:

$$\frac{dx_i}{dx_e}=F_{ij}(k_j,\ x_i,\ x_e).$$

Paralleelsete ja järjestikuliste reaktsioonide suhtelised kiiruskonstandid ($k_j$) määratakse raalil arvutatud komponentide kontsentratsioonide ($x_i$, $x_e$) väärtuste lähendamisel katseandmetele.

On käsitletud keerulise liitumis- ja isomerisatsioonireaktsiooni näite varal konversioonimudeli koostamist, selle vahendusel sihtainete saagise optimeerimist ning üleminekuvõimalusi reaktsiooni kineetikavõrrandeile.



*К. ЛЭЭТС*


## К КОЛИЧЕСТВЕННОМУ МОДЕЛИРОВАНИЮ ХИМИЧЕСКИХ РЕАКЦИЙ

### 1. О количественном подходе к изучению сложных органических реакций. Конверсионная модель реакции


Представлен новый методологический подход для количественного моделирования сложных реакционных систем, включающий определение материальных балансов компонентов в ходе реакции в зависимости от соотношения и степени конверсии ингредиентов.

Получаемые опытные данные переводят в графические интегральные конверсионные модели, на основе которых составляют систему дифференциальных конверсионных уравнений реакций:

$$\frac{dx_i}{dx_e}=F_{ij}(k_j,\ x_i,\ x_e).$$

Численные значения относительных кинетических констант для параллельных и последовательных реакций ($k_j$) находят аппроксимированием на ЭВМ расчетных значений концентраций к опытным ($x_i$, $x_e$). Составление конверсионной модели, оптимизация на ее основе выходов целевых продуктов, а также возможности перехода на кинетические уравнения реакции обсуждены на примере сложной каталитической реакции присоединения и изомеризации.