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New Approaches to the Analysis of the Elementary Reactions Kinetics

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We consider an alternative implementation of reaction progress kinetic analysis based on physically rigorous models of chemical kinetics. In addition we investigate the adaptation of dimensional kinetic constants of the classical chemical kinetics models for use in physically rigorous ones.

Keywords: reaction progress kinetic analysis, elementary reactions.

Introduction

In the course of this work we have considered the realisation of reaction progress kinetic analysis based on the alternative model of chemical kinetics from article [1]. Under the term RPKA (reaction progress kinetic analysis) we will imply a complex process of studying the mechanism of reaction, which can be divided roughly into four stages.

The first stage of RPKA process amounts to finding a set of initial conditions and temperature modes for the reaction of interest, which will enable to study the kinetics in a wide spectrum of dynamical regimes.

In the second stage the reaction is being repeatedly reproduced in the laboratory for selected initial concentrations and temperature modes. In the course of all this reactions the intermediate values are recorded for concentrations of the reagents.

In the third stage the concentrations of the reagents are used for the formalization of models of chemical kinetics: calculation of the kinetic constants, activation energies, and so on.

In the fourth stage the verification of the predictions for the constructed model of kinetics is performed. Wherein, this check is done by selecting some new initial conditions and temperature modes and repeating the reaction with subsequent comparison of model predictions and experimental data. In case if the data disagree the model will be corrected and the checking step will be repeated.

The process of reaction progress kinetic analysis for the first time was fully described in the works of Donna Blackmond (see [2]). This process proved to be an extremely useful tool for the study of reactions, since it provided a much more accurate picture of the reaction kinetics in comparison to the classic methods of research. Note that for the application of the RPKA the selection of underlying mathematical *model of chemical kinetics* for the third stage of this process is of critical importance for research success.

In this article we will focus on **basic models of chemical kinetics** (examples in [3–6]). Their construction and initial analysis was done decades ago, and the obtained basic models have proven effective both in theoretical chemistry and in practice. However, due to the increased interest in the modelling of non-stationary processes[†] in catalysis, and biochemistry modelling in general there is a need to rethink and improve this basic models.

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[†]For rationale on the necessity to work primarily with the basic models in this context see [8].

All existing base models of chemical kinetics can be divided into two classes: regression and physical ones. **Regression** models are tend to use technical parameters and equations, which are generally either devoid of physical meaning, or just incorrect (examples in [3, 4]). One of the most common variant of the basic models of this technical direction are kinetic models with dimensional constants. For example, in case of reaction $A_1 + \dots + A_n \rightarrow B$ the equation[‡] of kinetics with dimensional constant k will be as follows:

$$\frac{d[B]}{dt} = k \cdot [A_1] \dots [A_n] \cdot e^{\left(-\frac{E}{R \cdot T}\right)} \quad [k] = \left[\left(\frac{m^3}{mol} \right)^{n-1} \cdot \frac{1}{sec} \right].$$

In such models, $[A_1], \dots, [A_n], [B]$ are the concentrations of reagents with dimension mol/m^3 , while the dimension of parameter k depends on the number of reagents n . The main problem of these models is the simplifying position that parameter k is constant. In fact, this leads to the abnormal description of kinetics, since the dimension of k assumes at least a dependence of this parameter on the volume of the reaction medium.

For basic kinetic models of alternative **physical** direction the main priority is the physical rigorousness of kinetic description. However, most of the classical models of this direction have a common set of problems that makes them fall short of being a fully physically rigorous (examples in [5–7]). We will consider the problems of this physical models with some specific examples. Let a reaction of form $k_1 B_1 + k_2 B_2 \rightleftharpoons k_3 C$ be elementary and reversible. The elementary rate of the direct step of this reaction we will denote as v^+ and the activation energy for the direct step as E^+ . Introducing a similar notation for the reverse step of reaction v^- and E^- we can estimate the number of reactions per time with the formulas (see (1.2) in [5]):

$$\omega^+(t) = v^+ e^{\left(-\frac{E^+}{R \cdot T(t)}\right)} e^{k_1 \mu_{B_1}(t) + k_2 \mu_{B_2}(t)}, \quad (1)$$

$$\omega^-(t) = v^- e^{\left(-\frac{E^-}{R \cdot T(t)}\right)} e^{\sum k_3 \mu_C(t)}, \quad (2)$$

where $\mu_s(t)$ is the chemical potential of substance s . In most models of this physical direction the chemical potential is expressed as logarithm $\mu_s = \ln[s]$, where $[s]$ is molar concentration of the substance $[s] = \nu_s/V$. Additionally, the molar concentrations of reagents are also commonly used in this models as the main variables in equations. For the considered reaction $k_1 B_1 + k_2 B_2 \rightleftharpoons k_3 C$ those are $[B_1]$, $[B_2]$ and $[C]$ respectively. Finally the equations for the dynamic of this elementary reaction will take the following form (see (1.5) in [5]):

$$\frac{d[B_i]}{dt} = k_i \cdot (\omega^-(t) - \omega^+(t)), \quad i = 1, 2;$$

$$\frac{d[C]}{dt} = k_3 \cdot (\omega^+(t) - \omega^-(t)).$$

Substituting the formulas (1) and (2) in this equations, and using the chemical potential $\mu_s = \ln[s]$ it is easy to see that resulting equations will have unbalanced dimensions

$$\frac{d[C]}{dt} = v^+ \cdot [B_1] \cdot [B_2] \cdot e^{\left(-\frac{E^+}{R \cdot T(t)}\right)}, \quad \left[\frac{mol}{sec \cdot m^3} \right] \neq \left[\frac{mol^2}{sec \cdot m^6} \right].$$

The simplest option to correct the inconsistency in dimension is by switching to the dimensional constants. However, this will lead to the classical regression models, which are obviously not physically rigorous.

Other part of classical models of physical direction are using volume fractions $[s]_d$ instead of concentrations as main variables and also to determine the chemical potential $\mu_s = \ln[s]_d$.

[‡]The derivations of this equation is based on the law of mass action and Arrhenius law.

Right sides of dynamic equations for this case will be defined almost correctly as $[s]_d$ in the first approximation actually gives the probability of detecting a single molecule s at some point in reaction medium. However, in such models there is a problem of matching equations in scale units. Both parts of the differential equation in this case have the same dimension, but different scale, and hence, such equations can yield incorrect values for the fraction $[C]_d > 1$ (see Fig. 1).

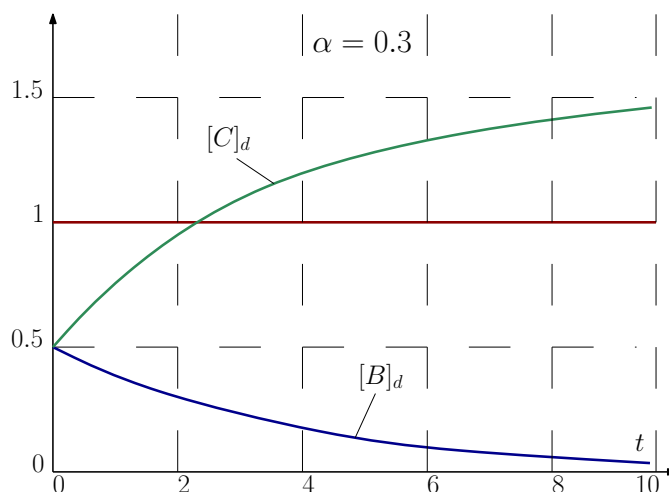


Fig. 1. Incorrect kinetic curves of decay reaction $B \rightarrow 2C$ for case of $\alpha = 0.3$

We can demonstrate this inconsistency in scale with a simple example of decay reaction $B \rightarrow 2C$. For simplification, we assume that the reaction is irreversible, and the rate of direct elementary stage is $v^+ = 1$. Then the equations for the reaction dynamics will be as follows:

$$\frac{d[C]_d}{dt} = 2[B]_d \cdot e\left(-\frac{E^+}{R \cdot T}\right),$$

$$\frac{d[B]_d}{dt} = -[B]_d \cdot e\left(-\frac{E^+}{R \cdot T}\right).$$

For simplicity, we can use the isothermal approximation and denote the exponential factor in the probability of the initiation of this reaction as $\alpha = e\left(-\frac{E^+}{R \cdot T}\right)$. As a result, the solution for a system of differential equations of chemical kinetics will be:

$$[B]_d(t) = [B]_d(0) \cdot e^{-\alpha t},$$

$$[C]_d(t) = [C]_d(0) + 2 \cdot [B]_d(0) \cdot (1 - e^{-\alpha t}).$$

It is easy to observe that incorrect state $[C]_d > 1$ in this case will be possible for any α from the valid range of $0 < \alpha \leq 1$.

Remark. In case if we drop the isothermal approximation for the reaction $B \rightarrow 2C$ the incorrect state will be achieved at a quicker pace, since under decay reaction due to the release of energy the rate of reaction is accelerating.

The third version of the basic models of chemical kinetics is based on the differential algebraic equations. The basic idea of this approach is to use the law of mass conservation in the form of the following equation (see (1.1.8) of the work [8]):

$$\sum_{i=1}^n m_{ij}[i] = b_j, \quad j = \overline{1, n}.$$

In this equation, b_j — denote the values of balance and $m_{i,j}$ will be proportional to the number of atoms of j type in the material of i type. The equation for the mass balance together with the condition of non-negative solutions allows to select a physically reasonable solution to the differential equation. However, the resulting model becomes cumbersome, as the use of additional algebraic equations for mass balance is not intuitive at all, since they should have been taken into account in the original differential equations.

In the framework of [1] we managed to build a basic chemical kinetics model that does not require any algebraic corrections to its equations. It should be noted that the construction of this model from [1] was in some part motivated by [5] and [8]. Still this basic model from [1] has one big flaw in kinetic description and thus cannot be considered fully physically rigorous.

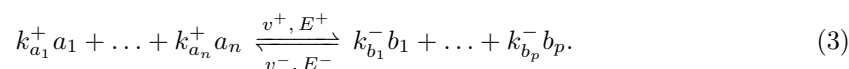
The novelty of the approach of [1] is in explicit introduction of a volume V of the reaction medium in the kinetic equations. This enables us to make the differential equations consistent both on the dimension and scale, and eventually to eliminate the use of the algebraic equations for the mass balance in model. Moreover, the basic model of the work [1] additionally focuses on correct description for the thermodynamics of reactions.

In addition to the basic model of the kinetics a generalized version of this model was introduced in the work [9] for reaction-diffusion systems.

The main objective of the current work is the correction of the model from article [1] and the adaptation of process of reaction progress kinetic analysis to use with chemical kinetics models from articles [1] and [9].

1. Description of the basic model of chemical kinetics

When working with reaction systems of chemical kinetics it is convenient to divide the molecules of this systems in two classes: independent substrates S and intermediates I . This is due to the fact that intermediates of chemical reactions I are short lived substances which are assigned some technical names derived from the names of the independent reagents and reaction steps. In article [1] we have taken similar approach and divided the set of all molecules of reaction system into two classes: S and I . Wherein, the set of chemical reactions for the considered reaction system in [1] is denoted as \mathcal{R} , where any reaction is $r \in \mathcal{R}$ is as follows:



The set of reaction r substrates is denoted as $A(r) = \{a_1, \dots, a_{n(r)}\}$ and the set of products is denoted as $B(r) = \{b_1, \dots, b_{p(r)}\}$. The coefficients $k^+(r)$ и $k^-(r)$ in formula (3) correspond to the stoichiometric coefficients of the reaction r substrates and products, while E^+, v^+ and E^-, v^- correspond to activation energies and base rates of forward and backward steps of r .

To construct the basic model of kinetics in the article [1] we for simplification of formalism have neglected:

- 1) the real distribution of molecules in space (it is considered uniform);
- 2) the finite rate of heat dissipation;
- 3) the exchange of energy and matter with the environment and change in pressure;
- 4) the phase transitions between aggregate states of matter;
- 5) the case of complex reactions.

Variables in the base model of chemical kinetics are the number of molecules $N_p(t)$ and the temperature $T(t)$ in the volume V , while their dynamics is described with a system[§] of differential equations of the following form:

$$\frac{dN_p}{dt} = \sum_{\substack{r \in \mathcal{R}: \\ p \in A(r)}} k_p^+(r) \cdot (\omega_r^-(t) - \omega_r^+(t)) + \sum_{\substack{r \in \mathcal{R}: \\ p \in B(r)}} k_p^-(r) \cdot (\omega_r^+(t) - \omega_r^-(t)); \quad (4)$$

$$\frac{dT}{dt} = \frac{1}{C} \cdot \sum_{r \in \mathcal{R}} (E^-(r) - E^+(r)) \cdot (\omega_r^+(t) - \omega_r^-(t)); \quad (5)$$

$$C = \sum_{s \in S} N_s(t) \cdot c_s(T) + \sum_{i \in I} N_i(t) \cdot c_i(T); \quad (6)$$

$$\omega_r^+(t) = v^+(r) \cdot e^{-\frac{E^+(r)}{R \cdot T}} \cdot \prod_{j=1}^{n(r)} \left(\frac{N_{a_j}(t)}{V \cdot \rho_{a_j}(T)} \right)^{k_{a_j}^+(r)} \cdot \min_j \left(\frac{N_{a_j}}{k_{a_j}} \right), \quad (7)$$

$$\omega_r^-(t) = v^-(r) \cdot e^{-\frac{E^-(r)}{R \cdot T}} \cdot \prod_{j=1}^{p(r)} \left(\frac{N_{b_j}(t)}{V \cdot \rho_{b_j}(T)} \right)^{k_{b_j}^-(r)} \cdot \min_j \left(\frac{N_{b_j}}{k_{b_j}} \right). \quad (8)$$

In the formulas (4)–(8) for all reactions $r \in \mathcal{R}$ we denote the number of reactions per unit time as $\omega_r^+(t)$, while the number of reverse step reactions for r we denote as $\omega_r^-(t)$. Wherein, R is gas constant and $c_p(T)$, $\rho_p(T)$ are molecular heat capacity and density, which are defined as fixed function of temperature T .

Remark 1. For substance p in gaseous state the critical density $\rho_p(T_c)$ at a temperature of evaporation of p should be used instead of function $\rho_p(T)$.

Remark 2. The main innovation of the model (4)–(8) is the explicit use of medium volume V for expression of the volume fraction: $[p]_d = N_p/(V \cdot \rho_p)$. This eliminates the need for dimensional constants and helps to obtain a physically rigorous model of kinetics. Article [1] had a major flaw, because it omitted coefficient $\min_j (N_{a_j}/k_{a_j})$ for the maximum number of reactions.

Remark 3. The second innovation of model (4)–(8) is the requirement of decomposition of all reactions to the elementary steps, which helps to ensure correct use of the total heat capacity C .

In general, when defining the model from [1] the choice of variables is not of principal importance. As an alternative to the number of molecules N_p in this role can act, for example, the molar concentrations $[p] = \nu_p/V$, as well as the volume fractions $[p]_d = N_p/(V \cdot \rho_p)$.

In particular, for the example decay reaction $B \rightarrow 2C$, which was considered in the introduction of this article, we can obtain the following system for the volume fractions:

$$\frac{d[C]_d}{dt} = \frac{2\rho_B[B]_d^2}{\rho_C} \cdot e^{-\frac{E^+}{R \cdot T}}; \quad \frac{d[B]_d}{dt} = -[B]_d^2 \cdot e^{-\frac{E^+}{R \cdot T}}.$$

If we again use the isothermal approximation and denote the exponential factor of the probability of the reaction initiation as $\alpha = e^{-\frac{E^+}{R \cdot T}}$, then the solution will take the form:

$$[B]_d(t) = \frac{[B]_d(0)}{\alpha t [B]_d(0) + 1},$$

$$[C]_d(t) = [C]_d(0) + \frac{2\rho_B}{\rho_C} \cdot \frac{\alpha t ([B]_d(0))^2}{\alpha t [B]_d(0) + 1}.$$

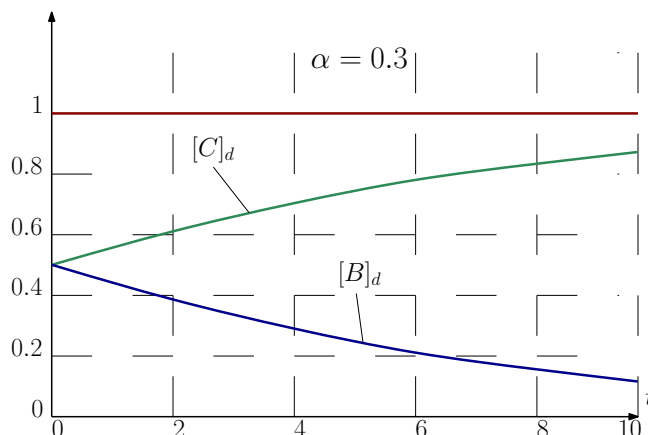


Fig. 2. Kinetic curves of decay reaction $B \rightarrow 2C$ for case of $\alpha = 0.3$

This solution will be correct if we choose physically adequate molecular density $\rho_C \approx 2\rho_B$ for the example reaction (see Fig. 2).

2. Transition from models with dimensional constants to physically rigorous models of chemical kinetics

In practice, the most commonly used are the models with dimensional constants (see examples [4] and [10]). We will consider the interconnection of model (4)–(8) and models with dimensional constants on the basis of two examples of elementary reactions.

Example 1. Let us consider the irreversible reaction of conversion $B \rightarrow C$ at $T = \text{const.}$ If we choose molar concentrations as variables $[p](t) = \nu_p(t)/V$, then we can write the following equation for model with dimensional constant k

$$\frac{d[C]}{dt} = k \cdot [B] \cdot e^{\left(-\frac{E^+}{R \cdot T}\right)}, \quad [k] = \left[\frac{1}{\text{sec}}\right].$$

Using the fact that the number of molecules $N_C(t) = \nu_C(t) \cdot N_A = [C](t) \cdot N_A \cdot V$, and denoting the molar density of B as ρ_B^V , we can write the following equation for model (4)–(8)

$$\frac{d[C]}{dt} = v^+ \cdot \frac{[B]^2}{\rho_B^V} \cdot e^{\left(-\frac{E^+}{R \cdot T}\right)}.$$

As a result, we obtain the equation which binds together constant k and elementary rate v^+

$$v^+ = k \cdot \rho_B^V / [B]. \quad (9)$$

Remark 4. Instead of molar density ρ_B^V in equation (9) one can use either the molecular density $\rho_B = \rho_B^V \cdot N_A$, or standard mass density $\rho_B^m = \rho_B^V \cdot M_B$, where M_B is a molecular mass of B .

Remark 5. Let us note that from the equation (9) it is implied that k is inversely proportional to the volume $k \sim 1/V$. This is just as expected, since according to simplifying position 1 of

[§]In the equation for the total heat capacity C in par with the reactants must also be included all inert substances which act as solvents for the reactants.

model (4)–(8) all substances are considered uniformly dispersed[¶] in the reaction medium. From a practical point of view, this means that for the transition to the model (4)–(8) from a model with a dimensional constant one will need to estimate the mean value of $[B] = \nu_B/V$ for the corresponding reaction.

A specific reaction that is close to the idealized scheme of example 1 is the reaction of hydrogen peroxide dissociation $H_2O_2 \rightarrow 2OH$ in the gas phase. The value of dimensional constant ($k = 10^{13}$ 1/c) for this reaction is given in [10] on page 139. The density of hydrogen peroxide according to remark 1 of paragraph 1 should be taken for the liquid phase: $\rho_{H_2O_2} = 1.44 \cdot 10^{-9}$ g/m³, and the molecular mass of H_2O_2 is respectively $M_{H_2O_2} = 34.01$ g/mol. Assuming that the measurement of constant k for the reaction $H_2O_2 \rightarrow 2OH$ in [10] was carried out in an autoclave of volume $V = 50$ m³ with mean value of $\nu(H_2O_2) = 100$ mol, we obtain:

$$H_2O_2 \rightarrow 2OH : \quad v^+ \approx \frac{k \cdot \rho_{H_2O_2}}{2 \cdot M_{H_2O_2}} \approx 2.117 \cdot 10^2 \frac{1}{c}.$$

Let us note, that for a more clear view, in addition to the pure speed of the reaction v^+ we can also estimate the molar rate v^+/N_A mol/c, which will be present in the equation for the dynamics of the amount of substance H_2O_2 .

Example 2. Let us consider the irreversible reaction of synthesis $B + C \rightarrow D$ under isothermal approximation $T = const$. If we choose molar concentrations as variables $[p](t) = \nu_p(t)/V$, then we can write the following equation for model with dimensional constant k :

$$\frac{d[D]}{dt} = k \cdot [B] \cdot [C] \cdot e^{\left(-\frac{E^+}{R \cdot T}\right)}, \quad [k] = \left[\frac{m^3}{mol \cdot sec} \right].$$

We can write the following model equations (4)–(8) for this reaction by analogy to example 1:

$$\frac{d[D]}{dt} = v^+ \cdot \left(\frac{[B]}{\rho_B^\nu} \right) \cdot \left(\frac{[C]}{\rho_C^\nu} \right) \cdot e^{\left(-\frac{E^+}{R \cdot T}\right)} \cdot \min([B], [C]).$$

As a result, we obtain the following equation, which links constant k and elementary rate v^+

$$v^+ = k \cdot \rho_B^\nu \cdot \rho_C^\nu / \min([B], [C]). \quad (10)$$

The expression for v^+ is almost identical to the equation (9) for the first example, with the exception of featuring two molar densities ρ_B^ν and ρ_C^ν .

A specific reaction that is close to the idealized scheme of example 3 is the reaction of butane recombination $C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$ in the gas phase. The value of dimensional constant ($k = 3.5 \cdot 10^{11}$ mol/c) for this reaction is given in [10] on page 138, and the molecular weight of the ethyl group C_2H_5 is $M_{C_2H_5} = 29.05$ g/mol. The density of the ethyl group C_2H_5 in the liquid phase could be approximately estimated as $\rho_{C_2H_5} \approx 0.56 \cdot 10^{-9}$ g/m³. We use data on the density of matter in the liquid phase to satisfy remark 1 from paragraph 1 of this article. Assuming that the measurement of constant k for the reaction $C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$ in [10] was carried out in an autoclave with mean value of $\nu(C_2H_5) = 100$ mol, we obtain:

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10} : \quad v^+ \approx 0.5 \cdot k \cdot \left(\frac{\rho_{C_2H_5}}{M_{C_2H_5}} \right)^2 \approx 65 \cdot 10^{-11} \frac{1}{c}.$$

[¶]If it is not, and the dissolution of one or more substances in the volume goes in parallel with the reaction, than one should use instead a reaction-diffusion model like [9].

3. The formalization of elementary reactions with reaction progress kinetic analysis

In the paper [1] was considered a hierarchical algorithm of formalization for arbitrary reaction systems. This algorithm reduces the analysis of sophisticated reaction systems to the analysis of elementary reactions, which can occur in those systems. However, the formalization of individual elementary reactions within [1] was not considered in detail. Therefore, in this paper we demonstrate how to adapt the reaction progress kinetic analysis for the formalization of elementary chemical reactions on the basis of physically rigorous model (4)–(8).

Without the loss of generality, we assume that during the course of the reactions the number^{||} of molecules N_p are measured as an experimental data. We will start the description of adapted RPKA process by defining a set of basic parameters of a measuring apparatus, and then define the procedure of acquiring the experimental data.

Definition 1. *A set of basic parameters of a measuring apparatus consists of five coefficients $(\Delta N, \Delta T, T_{-\infty}, T_{+\infty}, t_{\infty})$, where*

- 1) ΔN – the absolute error of measurement of the number of molecules;
- 2) ΔT – the absolute error of measurement of the temperature;
- 3) $[T_{-\infty}, T_{+\infty}]$ – the range of values of temperature;
- 4) t_{∞} – the maximum duration of the experiments.

Definition 2. *Under the reading and preprocessing of experimental data we will imply a procedure for which*

- the **input data** are the set of time values t_0, t_1, \dots, t_n , the initial numbers $N_p(t_0)$ of reagents for all p and initial temperature $T(t_0)$;
- the **implementation** amounts to carrying the reaction under controlled conditions with the registration of $N_p(t)$ and $T(t)$ for all time values t_1, \dots, t_n ;
- the **output data** are the numbers $N_p(t_1^*), \dots, N_p(t_k^*)$ for all reagents p and temperatures $T(t_1^*), \dots, T(t_k^*)$, where (t_1^*, \dots, t_k^*) is a subsequence of (t_1, \dots, t_n) , which is obtained by eliminating all t_j : $|N_p(t_j) - N_p(t_{j-1})| < \Delta N$ for all p .

The algorithm for the recursive analysis of reaction in application to the formalization of the physically rigorous model (4)–(8) can be divided in five stages.

Stage 1. We will assume that time values are $t_0 = 0$, $t_n = t_{\infty}$, and all other time values t_j are uniformly distributed in interval $[t_0, t_n]$. Wherein, the total number of time samples n will be chosen arbitrarily $n \simeq 10 - 20$. As the initial data for the procedure of reading and preprocessing of experimental data we will choose room temperature $T(t_0)$ and equal values for all numbers $N_{p_1}(t_0) = \dots = N_{p_l}(t_0) = N_0$.

Stage 2. We implement the procedure of reading and preprocessing of experimental data (see definition 2 of this paragraph) for initial conditions from stage 1. As an output we will receive a set of values $N_p(t_1^*), \dots, N_p(t_k^*)$ for all p , and temperatures $T(t_1^*), \dots, T(t_k^*)$. In case $k < 2$, then we change the initial temperature $T(t_0) + 10 \cdot \Delta T$ and iteratively repeat the procedure while the number $k < 2$ and the temperature is $T < T_{+\infty}$.

Stage 3. If we failed to find the appropriate temperature conditions on stage 2, then we assume that reagents are inert. Otherwise, we obtain a set of values $N_p(t_1^*), \dots, N_p(t_k^*)$ for all

^{||}For the alternative cases: the amount of matter $\nu_p = N_p/N_A$, the molar concentrations $[p] = \nu_p/V$ and volume fractions $[p]_d = [p]/\rho_p^0$, we can easily convert them to the number of molecules N_p and vice versa.

molecules p and a set of temperatures $T(t_1^*), \dots, T(t_k^*)$, where $k \geq 2$. We will continue the iteration process by changing the initial temperature $T(t_0) + 10 \cdot \Delta T$ and repeatedly carrying out the reaction until we get more data $N_p(t_1), \dots, N_p(t_l)$ for all p , which will be different from $N_p(t_j^*)$ to a value greater than ΔN for at least two coincident time counts.

Stage 4. The values obtained in stages 2 and 3 will be used to estimate the parameters v^+, E^+, v^-, E^- of model (4)–(8) with least squares approximation** on the basis of difference equations for N and T . For example, for the reversible reaction of conversion $B \rightleftharpoons C$ the difference equations for number N_C will take the form:

$$\frac{N_C(t_{j+1}) - N_C(t_j)}{t_{j+1} - t_j} = v^+ \cdot e^{\left(-\frac{E^+}{R \cdot T(t_j)}\right)} \cdot \frac{N_B(t_j)^2}{\rho_B \cdot V} - v^- \cdot e^{\left(-\frac{E^-}{R \cdot T(t_j)}\right)} \cdot \frac{N_C(t_j)^2}{\rho_C \cdot V}.$$

Stage 5. We carry out the checking of the formalized model. At first, we calculate the mean square error of modelling the dynamics of already obtained experimental data. If this error is less than ΔN , then we conduct an additional experiment by changing the initial numbers $N_p(t_0) \pm 50\Delta N$ and carrying out reaction for the same initial temperatures. If the check reveals that the mean square error is greater than ΔN , then the model (4)–(8) is not suitable to describe the reaction of interest. This means that either the reaction has intermediate steps or the distribution of the reagents during the reaction cannot be neglected.

Remark 1. It should be noted separately about the so-called non-Arrhenius reactions (for examples see [11]), which stated to violate the exponential dependence of kinetics from temperature. Such sophisticated temperature dependence in this case is realized by hidden^{††} competing parallel reactions. Thus, without loss of generality, we can assume that elementary non-Arrhenius reactions do not exist.

Remark 2. The formalization of complex reactions was considered in the framework of [1]. The algorithm of formalization that was proposed in [1] could also be integrated into the RPKA process for arbitrary reaction systems.

Conclusion

When using the models of chemical kinetics in practice, quite often it is impossible to ensure uniform distribution of the reactants^{‡‡} in the reaction medium. Likewise, the reactions which were initially supposed to be elementary, may actually have one or more quick intermediate stages. Therefore, we will consider how in practice the RPKA process could be adapted for these two cases.

Alternative 1. If one wants to adapt RPKA process to formalize reaction-diffusion model, similar to [9], it will require to approximately estimate the distribution of the reactants in the reaction medium (for example, using magnetic resonance imaging). Also, the formalization will require either the diffusion coefficients D_p of reagents, or solubility parameters.

Alternative 2. To adapt the RPKA process to formalize the model (4)–(8) in the case of complex reaction one would need to estimate the density ρ_i and the heat capacity c_i of all intermediate products of individual stages of this reaction. The evaluation of the heat capacity c_i can be performed by conducting reaction for a number of temperature regimes and then by applying the least squares method to difference equations for (4)–(8). In turn, for the experimental evaluation of the intermediate product density ρ_i one of the following methods could be used.

**As soon as on stages 2 and 3 we have obtained values for at least two different temperature modes, the method of least squares will be able to separate linear factors v^+ and v^- from exponential ones E^+ and E^- uniquely.

††In most cases, the competition happens with the decay reaction for some reagents of initial reaction.

‡‡For example, in the case of slow solubility of reagents in used solvent.

1. If the volume of the reaction medium is fixed and occupied by liquid, then the density of intermediate products can be estimated by simultaneously assessing the concentration and pressure change during the course of the reaction.
2. If in the reaction medium a gas is mixed with liquid, then to estimate the density of intermediate products one can simultaneously investigate the dynamics of liquid's volume with the change of concentrations of reagents.

After obtaining the additional data, it is still required to use the least squares method to finally estimate the density ρ_i of intermediate products.

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Новые подходы к анализу кинетики элементарных химических реакций

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Рассмотрен альтернативный способ реализации процесса кинетического анализа хода реакций РPKA на основе физически строгих моделей химической кинетики. Дополнительно были исследованы варианты адаптации размерных кинетических констант классических моделей химической кинетики для использования в физически строгих моделях.

Ключевые слова: кинетический анализ хода реакции, элементарные реакции.