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Study of Converse Problems in Chemical Kinetics as a Method for the Investigation of the Mechanisms of Complex Reactions

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The application of mathematical modelling methods to the determination of the mechanisms of complex chemical reactions is considered. On the basis of the analysis of the present state of the mathematical modelling of chemical kinetic processes, it is shown that the study of converse problems constitutes an extension of the traditional kinetic approach to the construction of models. A classification of the direct and converse problems in chemical kinetics is proposed. It is shown that converse problems are of greatest interest at the present time in the identification of the chemical type of the reaction mechanism. The bibliography includes 133 references.

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I. INTRODUCTION

The determination of the mechanisms of chemical processes is a complex physicochemical problem, whose solution is based on the fundamental postulates of theoretical chemical kinetics and on experimental studies.[1-3] The development of computer techniques and progress in the mathematical methods used in chemistry have altered qualitatively the role of mathematical modelling in the solution of this problem, having converted it into a method for the investigation of the mechanisms of chemical reactions just as legitimate as other procedures.[4-6] However, in most studies on the application of mathematical modelling in chemical kinetics,[7-15] mainly probability-statistical and computational aspects of the problem of the construction of models are considered and due attention is not paid to the kinetic aspect. The present review is devoted to the analysis of the present state of precisely this, kinetic aspect.

II. STUDY OF CONVERSE PROBLEMS IN CHEMICAL KINETICS AS A DEVELOPMENT OF THE KINETIC APPROACH TO THE CONSTRUCTION OF MODELS

One of the main ways of investigating the mechanisms of chemical reactions involves the kinetic approach.[16,17] The term reaction mechanism has usually come to be understood as the set of chemical stages making up the process.[5,18] In a broader sense, the word mechanism includes fundamental kinetic characteristics of the process such as the determination of the active species in the reaction, the ratios of the rates of the individual stages, etc.[4,13,19-22] (to make the treatment concrete, this type of mechanism has been called[22] the kinetic type of reaction mechanism).

The modelling method in the kinetic approach is based, on the one hand, on the kinetics of reactions of different classes and, on the other, on experimental design, which makes it possible to isolate and investigate quantitatively certain small fragments of the overall kinetic scheme.[4,17] A logical application of this approach permits the determination of the mechanism of the entire process, including the kinetic parameters of the stages. Indeed the majority of the mechanisms known at the present time have been deduced in precisely this way.[8-10,17,23] The success of this method has been to a large extent associated with the development of ideas about radical chain reactions.[1,24,25]

The modelling procedure in the kinetic approach includes three main stages:[4,5,17,22,26] (1) the purposeful collection of information, including the establishment of a tentative kinetic scheme process; (2) the selection of experimental methods on the basis of data obtained in the first stage and the design and carrying out of the experiment; (3) the kinetic-mathematical analysis. The application of the methods of computational mathematics and of the qualitative theory of differential equations in all the three stages of the modelling process[9] made it possible to isolate as the object of study a kinetic model of the process (i.e. a system of differential chemical kinetic equations).[17,27] The problems involved in the construction of such models reduce to problems involving the recovery of the right-hand sides in the systems of differential equations, which have come to be called the converse problems in mathematical physics.[28-30] Thus the converse problems in chemical kinetics are, in a broad sense of the term, problems involved in the determination of the reaction mechanism.[9,17,31] In essence, the converse problems involve the extension of the kinetic approach to processes whose models cannot be investigated without using computer techniques.

The specific content of each stage in the study of the mechanism is determined in the first place by the aim of the mathematical model.[5] Accordingly, it is possible to distinguish two large classes of converse problems;[32] the first class includes the converse problems whose study is used as a method for the investigation of the mechanisms of complex chemical reactions and the second includes converse problems in which mathematical models are a means for the solution of practically important problems of control, optimisation, prediction, etc. (target converse problems).

The traditional formulation of the converse problems in chemical kinetics[4,17,18,32,33] assigns primary importance to the rate constants for elementary reactions. It is assumed that, provided that the values of all the constants are known, the mathematical model of the process is defined and can be used for the solution of the target problems. For reactions of

simple types, such formulation of the problem[18,35] is correct and the problems involved in setting up mathematical models, in the determination of their adequacy, and in the estimation of the parameters are in essence solved simultaneously.

However, one should not apply mechanically such formulation of the converse problem in the consideration of reactions of complex types (chain, autocatalytic, and such processes) also because, in relation to complex processes, the converse problems are solved as a rule under conditions of an acute deficiency of experimental data, as a result of which the solutions obtained are ambiguous.[4,17-22,33-36] This ambiguity has in fact led at one time to a natural lack of confidence by experimenters in the results obtained from the solution of converse problems.[33,35] Evidently the ambiguity of the solution obtained can be eliminated by improving only the experimental technique and not the numerical method.[30] Thus some modification of the formulation of the converse problems is essential.[30]

In the first place, we may note that the formulation of the converse problem for reactions of complex types should vary depending on the aim in constructing the model and on the amount of *a priori* information about the process mechanism. Thus, for processes whose kinetics are known beforehand (i.e. with a known kinetic type of reaction mechanism[22]), the aim of the investigation is the determination of the unknown rate constants. In this case special kinetic experiments are used to solve the problem.[4,18,23,33,37-40] As a rule, the use of such problems is correct when the amount of experimental data is sufficient. The necessity to develop special experimental techniques for virtually each specific problem, their uniqueness, and high cost led to their comparatively rare employment when the aim of the study is to obtain a mathematical model of the process reflecting adequately the main kinetic features. In this case experimental methods are used to solve the problems whereby one can record the kinetics of the changes in the concentrations of comparatively stable reaction components[4,18] or to measure the steady-state reaction rates.[4,8,10-14] In this situation the mathematical model of the process is not determined by the rate constants themselves but by certain combinations of the latter,[9,10,17-23,41-46] whose determination can sometimes be the aim of the solution of the converse problem—the identification of parameters.[42]

The main deficiency of the kinetic approach when such experimental information is available consists in the fact that the measurements refer to the rates of slow stages and do not yield information about the rates and presence of faster stages,[48] i.e. about the kinetics of conversion of the active components of the reaction. Evidently, in the absence of *a priori* information about these kinetic features, the formulation of the problem of the parametric identification becomes pointless and the problem of the identification of the mechanism (more precisely the kinetic type of mechanism) of the reaction comes to the fore. Indeed, the kinetic scheme of the process contains no information about the reactivity of the reaction components and about the relative contributions of the stages to the overall process. In the absence of such information, it is impossible to isolate beforehand the combinations of constants determining the course of the process. Accordingly, there is also a change in the specific aim of the study, which consists in this instance in the determination of the kinetics, i.e. of the possible reaction mechanism.[13,21,26]

The most obvious way of obtaining information necessary for the determination of the possible mechanism consists in a direct experimental measurement of the varying concentrations of the intermediate reactive reaction components. However, as already stated, the high cost and complexity of the methods limits significantly the applicability of this approach.[4,17,23,37,49] The availability of experimental methods whereby the kinetics of the conversion of the "slow" reaction components or the steady-rates of the stages can be recorded has made such an experiment the main procedure for the determination of the possible reaction mechanism. The dependence of the initial or steady-state rates, induction periods, and other macrokinetic parameters under experimental conditions, for example, on the initial concentrations, does indeed frequently permit the determination of the reaction mechanism[8-15,23] on the basis of which it is possible to set up an adequate mathematical model.

The converse problems in chemical kinetics, which result from the natural extension of the kinetic approach, possess not only all the advantages but also all the disadvantages of the latter. Within this framework, it is impossible to demonstrate that the true reaction mechanism has been established[48] and one can only speak of the lack of contradiction between the mathematical model, corresponding to the mechanism obtained, and the existing experimental data,[4,19] i.e. of the possibility that such a mechanism can occur. The term "identification" should also be understood in precisely this sense.

The mathematical and computational aspects of the problem have been described fairly completely in the literature and here we shall specify only certain problems of a mathematical character, whose solution determines the real possibility of formulating the converse problems of chemical kinetics: (1) experimental design;[13,30,42,49,50] (2) the choice of the functional determining the similarity between the experimental and calculated values of the observed variables;[26,42,50-54] (3) the selection of a method for the integration of the system of potential chemical kinetic equations;[4,13,17,20,26,55-63] (4) the selection of a method for the minimisation of the functional.[4,11,13,19-21,42,50,52-55,63-74]

III. DIRECT PROBLEMS IN CHEMICAL KINETICS

In chemical kinetics the course of the process is determined by the time variation of the concentrations of the reactants. This dependence constitutes the information obtained from the study of the chemical process. The derivation of this information by the mathematical modelling of the chemical process is understood as the direct problem.[18] To make the treatment concrete, we shall consider processes for which the variation of the concentrations of the reactants (x) is specified unambiguously by the Cauchy problem:

$$\frac{dx}{dt} = f(x);\ x(0) = x^0. \qquad (1)$$

This system[6,17,27] constitutes a kinetic model of the chemical process. The form of the right-hand side of Eqns.(1) is determined by a set of kinetic postulates,[17,75] which can be formulated in the following manner for the processes involved in isothermal equilibrium chemical kinetics in closed systems and which are mainly considered in this review.

1. The chemical process can be represented by a set of elementary stages:

$$\sum_{i=1}^{N} \nu_{ij}^{+} A_i \rightarrow \sum_{i=1}^{N} \nu_{ij}^{-} A_i;\quad j = 1, 2, \ldots, M, \qquad (2)$$

where A_1, A_2, ..., A_N are the components participating in the reaction and ν is the stoichiometric matrix ($\nu_{ij} = \nu_{ij}^{+} - \nu_{ij}^{-}$; the plus and minus signs correspond to the stoichiometric coefficients of the reactant entering into the jth reaction and formed in it).

2. The relation between the rate of the elementary stage w_j and the concentrations of the reactants involved in it, $x_i = [A_i]$, is determined by the Law of Mass Action:

$$w_j = k_j \prod_{i=1}^{N} x_i^{\nu_{ij}^+} , \qquad (3)$$

where k_j is the rate constant for the jth stage.

3. The overall rate of conversion of the jth reactant is determined by the principle of the independence of the occurrence of the elementary stages:

$$\frac{dx_i}{dt} = \sum_{j=1}^{M} \nu_{ij} w_j \qquad (4)$$

Thus, for the situation considered, the kinetic model of the process is specified by (1) the stoichiometric matrix ν and (2) by the initial concentrations and the rate constants.

The kinetic model should reflect the asymptotic character of the chemical process (the rapid attainment of steady-stage regimes with respect to the concentrations of the active reactants and the negligible contribution by the rates of certain stages to the rates of change in the concentrations of the reactants). We shall put Eqn.(1) in the following form:

$$\tau_i \frac{dx_i}{dt} = \varphi_i(x, k); \; i = 1, 2, \ldots, N; \qquad (5)$$
$$x(0) = x^0 ,$$

where

$$\varphi_i(x, k) = \sum_{j=1}^{M} H_{ij} \nu_{ij} w_j . \qquad (6)$$

Here $k = (k_1, k_2, \ldots, k_M)$ is the rate constant vector and τ_i and H_{ij} are parameters. We may note that Eqn.(1) is a special case of Eqn.(5) when $\tau_i = 1$ for all i and the elements of the matrix H_{ij} are determined for non-zero ν_{ij} and are unity.

We shall define the kinetic model as a special model in relation to Eqn.(1), provided that there exist parameters τ and H in Eqn.(5) such that, when $\tau_s \to 0$ ($s = p + 1, \ldots, N$) and $H_{mn} \to 0$, the system of Eqn.(1) is converted into a system

$$\frac{dx_i}{dt} = \varphi_i(x, k); \quad i = 1, 2, \ldots, p ,$$
$$0 = \varphi_i(x, k); \quad i = p+1, \ldots, N \qquad (7)$$

such that, over a certain time interval $t \in (t_1, t_2)$ and in a certain range of initial concentrations $x^0 \in X$, the following inequality holds:

$$|x(t) - \tilde{x}(z)| < \varepsilon , \qquad (8)$$

where $\tilde{x}(t)$ is the solution of Eqns.(7) and ε is a certain specified accuracy [for example the accuracy of the numerical integration of Eqn.(1)]. For convenience, we assume that the method of steady-state concentrations is applicable to the last $N-p$ reactants. The parameters H_{mn} will be set equal to zero, provided that the rate of the nth stage in the mth equation can be neglected.

We set up[32,42] a correspondence between the observations vector $\eta(t)$, in which account is taken of both the incompleteness and errors of the measurement, and the vector $x(t)$, which is a solution of Eqns.(1) or (7):

$$E(\eta(t)) = Rx(t) , \qquad (9)$$

where E is the symbol of the mathematical expectation of a random quantity and R a square matrix. In the general case, for example, in spectrometric measurements, the matrix R can be non-diagonal and can include spectral parameters. However, the matrix R is fairly often diagonal, i.e. measurements are made of the concentrations themselves and the diagonal elements of R are identical with the parameters of the vector τ or rank$(R) < N - p$. This situation will in fact be mainly analysed in the present review.

The procedure where the vector $\eta(t)$ is brought into correspondence with the vector-function $f(x, k)$ set up on the basis of Eqns.(1) will be referred to as the general direct problem and will be regarded as complete if rank$(R) = N$; otherwise it will be regarded as truncated.[32] The procedure in which the vector $\eta(t)$ is brought into correspondence with the vector-function $\phi(x, k)$ set up on the basis of Eqns.(7) will be referred to as the special direct problem.

Thus each direct problem is determined by the rules governing the construction of the right-hand sides of the equations, the stoichiometric matrix, the kinetic parameters and the law (R) relating the exact solution $x(t)$ to the observations vector $\eta(t)$.[32] For special direct problems, an essential intermediate link between the rules governing the construction of the right-hand sides, including the specification of the stoichiometric matrix, and the rules determining the kinetic parameters and the law (R) is the rule according to which the transition to the system of differential-algebraic Eqns.(7) is effected.

Evidently, depending on the values of the rate constants, the selected time interval, and the initial concentration range, different special problems correspond to the solution of the general problem [in the sense of the fulfillment of inequality (8)]. For this reason, before formulating the converse problem, we shall consider the classification of special kinetic models.

IV. SPECIAL KINETIC MODELS

We shall divide the kinetic models into two large classes. For models of class 1 (referred to by convention as the "chain" class), there are no linearly dependent equations among the algebraic components of Eqns.(7). For models of class 2 (the "catalytic" class), certain algebraic equations in the system (7) are linearly dependent. From the standpoint of kinetics, this means that a stationary regime with respect to the concentrations of the initial reactants is not established in "chain" processes, while in "catalytic" processes there is a possibility of the attainment of a stationary regime with respect to the concentration of the catalyst, which is a starting material. For "catalytic" processes, we eliminate from Eqns.(7) the linearly dependent equations and supplement the system by the material balance equations. Bearing in mind that certain concentrations involved in the material balance can be negligible, we introduce the parameters $\tilde{h}$ into the material balance equation. For example, in the case where the system contains one equation which is a linear combination of the remaining equations, we have

$$\sum_{i=p+1}^{N} \tilde{h}_i x_i = c^0 , \qquad (10)$$

where $\tilde{h}_i = 0$ provided that the concentration of the ith reactant in Eqn.(10) can be neglected, whilst otherwise $\tilde{h} = 1$ and c^0 is the initial concentration of the catalyst.

Evidently the selection of the elements of the vector τ and of the matrix H is not arbitrary in the general case. Thus τ_i can be zero only for intermediate reactants or the catalyst. Under these conditions, the choice of $\tau_i = 0$ determines to a large extent the choice of the elements of the matrix H. Indeed, in order that stationary conditions should

hold with respect to all the intermediate reactions, it is essential that the following system be soluble:[18]

$$\sum_{j=1}^{M} \nu_{lj}\mu_j = 0 \quad , \qquad (11)$$

where l are the numbers of the intermediate reactants (suppose that $l = p_1 + 1, \ldots, N$, where $p_1 < p$) and μ_j are the stoichiometric numbers of the stages.

The sum of the stages, taken with the corresponding stoichiometric numbers which are selected so that the overall stoichiometric reaction equation does not include intermediate species (for a stationary regime, the active intermediate species), is referred to as the reaction pathway[76-79] and determines a certain general kinetic model with lower dimensions:

$$\frac{dy}{dt} = \psi(y, x); \quad y(0) = y^0; \quad y = (y_1, y_2, \ldots, y_{p_1}) , \qquad (12)$$

where $y_i = x_i$ for $i = 1, 2, \ldots, p_1$.

Evidently the choice of the stochiometric numbers must ensure that Eqn.(11) holds for $l = p + 1, \ldots, N$ and does not hold for $l = p_1 + 1, \ldots, p$. Here the elements of the matrix H must be unity, provided that the corresponding $\mu_j \neq 0$ and must be zero in the opposite case. The elements of H not entering into the algebraic component of Eqns.(7) are selected arbitrarily.

We shall illustrate this procedure in relation to a catalytic reaction:[18]

	Stages	Pathways I	II	III
(1)	E + S → ES	1	1	2
(−1)	ES → E + S	1	0	1
(2)	ES → E + P	0	1	1

Here S is the substrate, E the catalyst, and P the reaction product. On the assumption of the stationary character of the reaction, the equation determining the stationary condition is

$$\mu_1 - \mu_{-1} - \mu_2 = 0 \qquad (13)$$

By choosing the smallest positive integral solutions of this equation, we find that three pathways (I–III) can be realised in the given system and that each pair of pathways is linearly independent.

We shall consider the balance equation

$$\tilde{h}_1[E] + \tilde{h}_2[ES] = [E]^0 . \qquad (14)$$

Evidently, three ways of selecting the parameters $\tilde{h}_i$ in Eqn.(14) are possible: (1) $\tilde{h}_1 = \tilde{h}_2 = 1$; (2) $\tilde{h}_1 = 1$, $\tilde{h}_2 = 0$; (3) $\tilde{h}_1 = 0$, $\tilde{h}_2 = 1$. Thus, in the given system nine special models will formally correspond to the single general kinetic model. For example, for the second pathway, the following special model exists:

$$\frac{dx_1}{dt} = -k_1 x_1 x_3 ,$$
$$\frac{dx_2}{dt} = k_2 x_4 ,$$
$$k_1 x_1 x_3 - k_2 x_4 = 0 ,$$
$$x_4 = x_3^0 ,$$

where $x_1 = [S]$, $x_2 = [P]$, $x_3 = [E]$, and $x_4 = [ES]$. The general kinetic model with lower dimensions corresponding to this special model then has the following form:

$$\frac{dx_1}{dt} = -k_2 x_3^0 ,$$
$$\frac{dx_2}{dt} = k_2 x_3^0 .$$

We may note that the determination of the general kinetic model with lower dimensions is possible only if the algebraic component of Eqns.(7) is soluble in an explicit form in terms of the concentrations of the reactants with respect to which a stationary regime is established.[19] However, the asymptotic character of the behaviour of kinetic systems increases significantly the probability of obtaining an explicit form of such models. For example, this has been achieved for extremely complex processes involving the joint oxidation of hydrocarbons.[80,81]

A definite asymptotic form of Eqns.(1) or a definite kinetic feature of the reaction corresponds to each set of numbers τ_i, H_{ij}, and $\tilde{h}_i$. A definite reaction regime has been brought into correspondence[80] with each asymptotic type of this kind. When the range in which the initial concentrations are specified or the degree of conversion is altered, the regime can change. The set of regimes which can be realised in the system for the specified rate constants determines the kinetic type of the reaction mechanism.[22] Evidently a certain region in the rate constant space, in which specific asymptotic properties of Eqns.(1) are manifested, corresponds to each kinetic type of reaction mechanism. This region has been defined[22] only for "chain" processes (in the form of the ratio of the rates of elementary stages).

The solution of the direct problems in chemical kinetics is comparatively rarely the aim in itself; these problems [like the mathematical problem of integrating Eqns.(1) or (7)] are usually a component of the converse problems. One can indicate only one important feature associated intrinsically with their solution: the elucidation of the question of which special kinetic models correspond to the general model [in the sense of the fulfillment of inequality (8)] when the rate constants are known or within a certain range of rate constants and for specified ranges of the initial concentrations and a specified time interval.[4,17,26,63,82,83]

In other words, this problem consists in determining the kinetic type of the reaction mechanism. For example, in the solution of the problem for the methane oxidation reaction, it has been shown[26,63] that, up to 1600–1700 K, the course of the process is determined by the chain reaction regime, while at higher temperatures it is determined by the free radical reaction regimes; for the ethane oxidation reaction,[84] the kinetic type of the reaction mechanism is determined by the regime in which degenerate branching is associated with the decomposition of performic acid or of the superperoxy-radical and not with the reaction $CH_2O^{\bullet} + O_2 \rightarrow HCO^{\bullet} + HO_2^{\bullet}$, as had been assumed earlier. Gontkovskaya et al.[85] considered five reaction regimes and Dimitrov[17] considered six reaction regimes in the combustion of hydrogen as a function of conditions. The reaction regimes in the liquid-phase oxidation of hydrocarbons have been investigated.[4,81,86] The direct problem has been solved[87,88] in order to test the correspondence between the approximate formula for the calculation of the inhibition period in the inhibited oxidation hydrocarbons, obtained on the basis of a special kinetic model, and the exact values of this quantity obtained by solving the general direct problem.

V. CLASSIFICATION OF THE CONVERSE PROBLEMS IN CHEMICAL KINETICS

If the direct problems are considered as problems of discovering one realisation $\eta(t)$ of a certain structure, determined by the rules governing the construction of Eqns.(1), (9) or (7), (9), then the converse problems can be naturally interpreted as the recovery of the elements

of this structure from the set of observations $\eta(t)$.[32] The rules governing the construction of the realisation $\eta(t)$ are regarded as statistical hypotheses.

We shall consider these hypotheses for isothermal chemical kinetic processes in which it is assumed that the following parameters are known: Π_1—the matrix for ν_{ij}; Π_2—the law relating the rate of the elementary stage to the concentrations, for example, Eqns.(3); Π_3—the expression for the total rate of conversion of all the reactants, for example Eqn.(4); Π_4—the limiting transition to which corresponds the the solution of the partial direct problem, or the absence of such a transition; Π_5—the kinetic parameters.

The system of hypotheses $\Pi_1-\Pi_5$ determines the general kinetic model and its corresponding special models. We shall supplement this system by hypotheses C, defining the model of observations, in which the following parameters are assumed to be known: C_1—the matrix R; C_2—the form of the distribution of experimental errors (with an accuracy to within the values of the parameters); C_3—the parameters of the distribution.

This system makes it possible to construct a hypothetical solution to the direct problem and to compare it with the existing set of experimental data $\eta(t)$. It is natural to consider the converse problems in chemical kinetics as problems of the recovery of the unknown hypotheses in this system from the known set of $\eta(t)$. The converse problems associated with the recovery of the hypotheses C_2-C_3 are outside the framework of this review. Their recovery requires as a rule the formulation of special statistical experiments.

The form of the matrix R is in most cases not known exactly. When different spectrometric measurements are performed, the matrix R frequently includes unknown parameters (for example, the absorption coefficients in spectrophotometric measurements[72]), which also have to be recovered in the solution of the converse problems. However, for simplicity, we shall assume that the matrix R is fully defined.

It is easy to note that, in the formulation of the direct problem, a hierarchy of hypotheses Π_i arises and consists in the fact that a definite content cannot be attributed to the hypothesis Π_s if the hypothesis Π_{s-1} has not been formulated. The pointlessness of formulating the converse problem as the problem of recovering the hypothesis Π_s when the hypothesis Π_{s-1} is unknown follows from the hierarchy of hypotheses. It is evident that, for example, the formulation of the problem of finding the rate constants has no significance if it is not known *a priori* whether the Law of Mass Action holds.

As a rule, having at ones disposal a set of observations, it is possible to state beforehand whether we are dealing with a complete [rank(R) = N] or truncated [rank(R) < N] solution of the direct problem. The situation is different as regards the question whether the above set of observations is a result of the solution of the general or special direct problems. In fact, in a real situation we are always dealing with a solution of the general problem and the limiting transition to the special problem is merely a mathematical reflection of the characteristic features of the chemical reaction.

We shall refer to the converse problem as general if it is known that there is no limiting transition in which it is impossible to distinguish the solutions of the general and special direct problems for a specified experimental accuracy. Otherwise we shall refer to it as a special converse problem.

The asymptotic character of the behaviour of chemical processes and the difficulty of the experimental measurement of the changes in the concentrations of all the reactants are due to the same physicochemical causes. The times during which the process begins to be determined by the special kinetic model amounts to millionths of a second (and less). This creates experimental difficulties in the study of the kinetics before the attainment of a stationary regime. Furthermore, in view of the high reactivity of the "fast" reactants, their concentrations are low (down to 10^{-12} M) and their experimental determination also gives rise to difficulties at the present time. Thus the deficiency of experimental data at the disposal of investigators in the solution of converse problems with deep physicochemical roots and the success of the solution are in many respects determined by the availability of *a priori* data on the process investigated.[22]

The extent to which the chemical process has been studied, i.e. the availability of information about $\Pi_1-\Pi_5$, determines the level of the converse problem.[32] The zero level corresponds to the case where all the factors constituting the direct problem, including the parameters, are known. The converse problem at this level consists in testing the consistency of the general or special kinetic model with the available set of experimental data. The converse problems at this level have been solved, for example, by Emanuel' and co-workers.[89-91] Evidently, whatever the level of the converse problem, the question of consistency is the first to which it is essential to obtain an answer in the course of its solution.

The usual formulation of converse problems as problems involving the determination of unknown kinetic parameters[5,14,17-22,26,35,41-45] on the assumption that information about $\Pi_1-\Pi_4$ is known beforehand belongs to the first level. A systematic approach[92] has been made[42] to the consideration of mathematical models of chemical kinetics. The term model is understood as a rule governing the transformation of the input variables into output variables, established by the analysis of causal-consequential relations:[93]

$$\eta(x(t)) = B\{t, \varepsilon, \theta\}, \qquad (15)$$

where $B\{.\}$ is an operator transforming the variables t, ε, and θ (where t is the time, ε are random factors, and θ are unknown parameters) into the observed variables η. Following the terminology proposed by Gorskii,[42] we shall define the converse first level problem as the problem of parametric identification arising in the case where the structure of the model, expressed by the operator $B\{.\}$, is known *a priori*. Otherwise, problems of structural identification arise—the converse problem at higher levels. The second level problems are associated with the recovery of hypothesis Π_4 for specified $\Pi_1-\Pi_3$, i.e. with the establishment of the kinetic type of the reaction mechanism.

The third and fourth level problems are associated with the recovery of the principal postulates of the chemical kinetics. In fairly numerous instances, for example, when reactions occurring under the conditions of a high density of the external energy flux (shock tubes, molecular beams, plasmachemical processes, etc. are considered), one cannot use the usual Arrhenius kinetics.[26,40,63] For a correct formulation of the kinetic postulates, it is essential to find the distribution of the excited species with respect to states. Thus the given problems refer to the generalised non-equilibrium chemical kinetics[94] and extend far outside the framework of the present review. Analysis of studies concerning non-equilibrium chemical kinetics has shown that, as a rule, the mathematical models for such processes are obtained within the framework of a physicochemical and not a kinetic approach.[17]

The fifth level problems are associated with the selection of one of several versions of the kinetic schemes for the process. If each such version (hypothesis) does not necessitate the reformulation of the fundamental postulates of chemical kinetics, a definite special kinetic model corresponds to it.

Thus in the case of equilibrium Arrhenius chemical kinetics, the second and fifth level problems actually refer to the same level.

1. Converse First Level Problems

When problems are considered at this level, account must be taken of the degree of completion and generality of the formulation of the direct problem with the aid of the solution of which a set of η_{ij} is believed to be obtainable. If a complete solution of the general direct problem is available, i.e. the kinetics of the variation of the concentrations of all the reactants in the time interval $t \in [0, T]$ have been determined experimentally, the problem has been correctly formulated.[34,36,45] The question of the validity of the formulation of the converse problem for the case where a truncated solution of the general direct problem is available (measurements are not made for all the reactants) or for the complete solution of the special problem (measurements are made for all the reactants in the stationary regime) can be elucidated for each specific problem. In the general case (truncated solution of the special problem), the formulation of the problem is as a rule incorrect.[4,17,18,20-22,33-36,41-45,95] From the physicochemical standpoint, such formulation is equivalent to an attempt to extract more information from experimental data than the latter contain.[4,19] Indeed the solution of the special truncated direct problem agrees in this case [in the sense that Eqn.(8) holds] with the solution obtained by the integration of the general kinetic model with lower dimensions [Eqn.(12)].

Thus the attempt to find all the rate constants reduces to the recovery of the concentration dependences for the "rapid" reactants which do not enter into Eqn.(12) at all.[41] From the mathematical standpoint, the causes precluding the solution of the problem in terms of the traditional formulation are as follows:[54] (1) the inadequate information extractable from the measurements; (2) a significant non-linearity of the kinetic models in terms of the constants being solved; (3) different sequences in the initial set of experimental data; (4) the lack of information about the fundamental statistical characteristics of the measurement. These causes are a consequence of the physicochemical characteristic of the processes (the asymptotic character of their behaviour), which were considered above.

Thus the solution of the problem of finding the rate constants gives rise to difficulties not as a result of any mathematical causes but by virtue of the complexity and the considerable labour involved in the extraction of sufficient experimental information.[19,20]

Regardless of the purpose for which the model has been constructed, the converse problem at the first level consists of two components:[20,21] the first significant component includes the test of the consistency of the proposed kinetic model with the available set η_{ij} of experimental data; the second, target component involves the extraction from the experiment of information about the process mechanism which is essential for the construction of the model. The fact that in the observation range the process is described by a special kinetic model and an umambiguous determination of the rate constants is therefore impossible clearly indicates a way of modifying the formulation of the converse problem. The first component of the problem then consists in finding a function from the class defined by Eqns.(1) which agrees [in the sense of Eqn.(8)] with the function from the specified class (7) providing the best description of the experimental data. The possibility of passing to a general model with low dimensions [Eqn.(12)] makes it possible in many instances to formulate the problem as one involving the finding of a function from the class defined by Eqn.(12). However, having solved this problem, it is essential to test whether rate constants having a physical significance, for which Eqn.(8) holds, do exist. Thus the first part of the converse first level problem can be formulated as follows: do parameters k or κ such that the kinetic model is not rejected for the given level of significance, actually exist? Hence follows the most frequently encountered formulation:[14,17,26] the aim is to find the parameters k or κ ensuring a maximum in the probability function.

Having solved the first part of the problem, it is possible, on the basis of the purpose for which the model has been constructed, to formulate the second part, which may consist in finding the unknown rate constant k or the unknown combinations of constants κ or the aim may be to reach a conclusion about the behaviour of the process.

2. Problems of Parametric Identification

The problem of finding unknown rate constants arises as a rule when a large amount of *a priori* information is available about the process, i.e. when many rate constants and some of their ratios are known. Special experimental kinetic studies are then performed,[37-39] which make it possible to estimate or revise a comparatively small number of constants. The vast majority of the values of the rate constants for elementary reaction known at present[35,96] have been obtained as a result of this approach.

For example, the aim of the study of the interaction of fluorine with halogens near the self-inflammation limit was the revision of the rate constants for the branching and energy chain termination reactions.[72] The experiments were performed under the conditions in the development of the branching-chain process, whose mechanism and the majority of rate constants were known.[97] The problem proved to be correctly formulated and the required parameters were estimated on a computer. An analogous investigation of the hydrogen combustion reaction[52] made it possible to revise four of the ten rate constants on the basis of the dependence of the maximum concentration of the radicals on the initial conditions. The solution of these converse problems does not give rise to fundamental difficulties. The methods developed[10,20,26,52,53,61,83,98] (see also the studies quoted by Gorskii[42]) have been applied successfully with this aim also in the study of reactions of simple types.[18,99,100]

The practically important properties of the process are often determined by the kinetics of the variation of the concentrations of the "slow" reactants. In this case the system of Eqns.(12) constitutes a model of the process and both parts of the converse first level problem can be combined in a single problem of the identification of the parameters κ. In many instances the parameters κ themselves determine the practically important properties of the process investigated and their determination is the aim of the solution of the converse problem, for example in tests.[101,102] This formulation of the converse problem also generally proves to be correct. Combinations of the rate constants have been estimated, for example, for the pyrolytic reactions of ethane,[20,61] the joint oxidation of hydrocarbons,[10,81,103] and the liquid-phase oxidation of tetralin [104] and in the study of the decomposition of hydroperoxides,[105] the initiated oxidation of hydrocarbons in the presence of inhibitors,[101,102] etc.

The formulation of the converse problem is used especially frequently in the study of heterogeneous-catalytic reactions. Thus the parameters κ have been estimated for the n-butene

dehydrogenation reactions,[106] the interaction of ethane with water vapour,[107] the hydrogenation of oxo-synthesis aldehydes,[108] the isomerisation of higher olefinic hydrocarbons,[109] the dehydrogenation of n-butane,[110] the hydrogenation of phenol [13] and benzene,[11] the oxidation of carbon monoxide,[111] etc. A more detailed bibliography on the solution of the converse problems in the study of heterogeneous-catalytic processes can be found in a number of other communications.[5-15,26,27,50]

The combinations of rate constants obtained can be used to revise the intrinsic rate constants using the results of the corresponding experiment or using *a priori* information about certain rate constants.[103]

3. Target Converse Problems

The situation where both parts of the converse problem are solved simultaneously[21,62] was considered in the previous subsection. The validity of the formulation of this problem ensures the uniqueness of the solution of the parametric identification problem. The availability of such solutions makes it possible to test the hypothesis about the adequacy of the process model. In the general case the transition to a general kinetic model with lower dimensions is not always justified: any set of constants satisfying the physical significance (or the specified form) of the special kinetic model and ensuring an adequate description defines a mathematical model which can be used to solve target problems.

As examples of the solution of the first part of the converse problem, we may point to studies on the modelling of the oxidation of tetralin,[104] the radiation-initiated isotope exchange of deuterium with the hydroxy-groups of silica gel,[26] the oxidation of methylacrolein,[112] the oxidation of ethylbenzene in the presence of aromatic amines and bivalent copper compounds,[113] the coupled oxidation of hydrocarbons,[114] the oxidation of coconut oil,[115] the sulphonation of secondary alcohols,[116] the catalytic oxidative dehydrogenation of n-butene,[117] the oxidative regeneration of aluminosilicate cracking catalysts,[118] the cyclooligomerisation of butadiene,[119] the oxidation of methanol,[120] the photochemical oxidation of polyolefins,[121] the oxidation of anthrahydroquinone,[122] the liquid-phase oxidation of *p*- and *m*-di-isopropylbenzenes,[123] the oxidation of carbon monoxide,[124] the hydrochlorination of acetylene,[125] etc. In these studies the rate constants were used solely as a means for the parametric test of the hypothesis of the adequacy of the corresponding mathematical models.

When the problem of adequacy has been solved positively and solution (1) has been found, one can proceed to the solution of a particular problem for which the mathematical model has been constructed. Formulation of such target problems will be considered in relation to kinetic prediction problems.[3,126] Suppose that one needs to test the truth of the claim that the target function $\phi[x(k)]$ belongs to the region u. For this problem, there may be three solutions: (1) "yes", i.e. $\phi \in u$ and the probability of the error is less than β, (2) "no", i.e. $\phi \notin u$ and the probability of error is less than α, and (3) the amount of experimental data for a well-founded answer for the specified α and β is small. Here α and β are respectively errors of the first and second kind.

4. Allowance for the *a priori* Information in the Solution of Converse First Level Problems

Evidently first level problems arise when sufficient *a priori* information is available about the process mechanism: the mechanism must satisfy a whole series of various requirements, which make it possible to formulate the hypotheses $\Pi_1-\Pi_4$. The need to take into account the *a priori* information in the formulation of converse problems has already been pointed out.[14,17,20,22,26] The range of parameters among which the solution has to be found is limited to certain control requirements from which the general control requirements, valid for any chemical reaction, and special requirements determined from the analysis of the available experimental data and *a priori* kinetic information, have been isolated. The general control requirements are believed to include[17] the Law of Conservation of Matter, the Law of Conservation of Energy, and the requirement that the concentration of any reactant at any instant is non-negative. In essence, these requirements constitute a test of the validity of the formulation of the kinetic scheme and the validity of the integration of Eqns.(1). In conformity with the terminology developed in the present review, we shall refer to the control requirements as general if they differentiate a certain class of special kinetic models, within the framework of which the "true" model is located, and we shall call them special if they differentiate one special model from this class.

The general control requirements are formulated on the basis of data obtained or available outside the formal kinetic approach to the construction of mathematical models and qualitative information about the process investigated which the investigator usually processes. We shall consider, for example, the consecutive chemical reaction[127]

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C .$$

Suppose that the variation of the concentration of substance C, corresponding to the solution of special direct problems, is determined experimentally:

$$[C](t, k) = [A]^0[1 - \exp(-k_{eff}t)]. \qquad (16)$$

In the absence of *a priori* information about the process mechanism, two special direct problems, defined by special control requirements, correspond to this solution: (1) $k_1 > k_2$ and (2) $k_1 \ll k_2$; accordingly, we have $k_{eff} = k_2$ or $k_{eff} = k_1$. The problem is formally outside the framework of the first level. In an informal consideration of A and B, the latter are real chemical substances and the possibility of the realisation of a particular special direct problem is determined in essence by the strength of the chemical bond in the corresponding molecules. Thus *a priori* information about the bond strength in the molecules of substances A and B makes it possible to formulate general control requirements within the framework of which the solution to the problem must be sought. For example, if the bond strength is greater in the molecule of substance A, then the general control requirement has the form $k_1 \ll k_2$. Analysis of semiquantitative data for the concentration of the intermediate B, which is not measured, leads to an analogous result. For example, when $\mathrm{Max}[B](t) \ll [A]^0$, we obtain $k_1 \ll k_2$ and $k_{eff} = k_1$. The regions corresponding to the existence of different kinetic types of mechanisms of the liquid-phase oxidation reaction of hydrocarbons in the oxidation of hydrocarbons inhibited by phenol have been related[128,129] to the R–H bond strength and temperature. For these classes of reactions, it is possible to isolate, on the basis of the bond energy and temperature, the general control requirements within the framework of which the converse problem should be solved.

Qualitative information about the process investigated may include at least two kinds of data:[22] (1) semiquantitative data on the yield of particular reaction products or the concentrations of intermediate reactants; (2) data concerning any effect observed in the system, for example, critical phenomena, the effect of inhibiting or initiating additives, etc. Formal mathematical treatment of such data makes it

possible to differentiate a system of general control requirements.

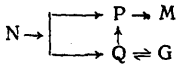
The question of the formal treatment of the control requirements ensuring the limitation of the region in which the converse problem is to be solved has been examined[14,22,26] but it is outside the framework of the present review. We shall only note that the control requirements must determine unambiguously the region in the rate constant space where the given special catalytic model of the process is realised.

Evidently the general control requirements unambiguously define the special kinetic model only for thoroughly investigated processes when a large amount of *a priori* physicochemical information is available. For example, such information has been obtained in the determination of the kinetics of the catalytic action of trinuclear clusters of the oxoacetates of the iron–chromium series in the model reaction involving the oxidation of ascorbic acid by hydrogen peroxide.[130] However the determination of such information is frequently associated, for example, in the study of pharmacokinetic reactions,[49] with serious experimental difficulties even for the example of consecutive chemical reactions considered above. Thus the problem of the identification of the kinetic type of the reaction mechanism—a converse second level problem—then comes to the fore.

VI. IDENTIFICATION OF THE REACTION MECHANISM

The ambiguity of the solution of the converse problem in terms of the traditional formulation is expressed, on the one hand, by the degeneracy of the minimum in the functional reflecting the similarity between the experimental and theoretical values of the observed variables, and, on the other hand, by the appearance of local minima in this functional. In both cases the ambiguity is caused by the deficiency of the experimental data, manifested in the asymptotic character of the system of differential Eqns.(1). Hitherto the formulation of the problem subject to the condition that the minimum in the functional is degenerate has been considered; we shall now deal with the formulation of problems involving the presence of local minima in the functional. The formulation of the converse problem as the problem of selecting the versions of the mechanisms agreeing well with the amount of experimental data arose as the natural response by investigators in the field of kinetics to the lack of validity of the traditional formulation.[93]

In the early studies the versions of the mechanism (the hypothesis about the mechanism) were special cases of a certain general kinetic scheme including all the process stages considered in the alternative versions of the mechanism.[13–15,26,57,101,102,131] For example, Peterson[131] considered eight alternative mechanisms of the oxidation of naphthalene and later Bard and Lapidus[50] considered thirteen such mechanisms, which are special cases of the general mechanism



where N is naphthalene, P phthalic anhydride, M maleic anhydride, Q naphthoquinone, and G gaseous products.

The need to formulate the problem by selecting the possible mechanism was dictated by the experimentally demonstrated lack of validity of the traditional formulation of the problem.[20,26] Indeed, if the formulation had been correct, then rate constants close to zero would have been obtained for stages which "do not occur" (the reactions take place at negligible rates) in the solution of the converse problems. However, even in the case of model problems[26] this was not found to be the case.

The presence of local minima in the functional in the case of mechanisms from which one cannot exclude any one stage necessitated an increase in the complexity of the concept of "version of the mechanism". Thus the ratios of the rates of individual stages[13,22] and different hypotheses concerning the reactivity of the intermediate reactants[20,22] have been included in this concept. It has been shown[22] that all these hypotheses are special cases of the description of experimental data by an asymptotic form of the complete system of differential Eqns.(1).

The need for the structural identification of kinetic models arises in the formal approach[20] to the study of any fairly complex process. Thus the model reaction involving the initiated chain consumption of a substance M with quadratic destruction of the active centre R, determined by the following kinetic scheme, has been considered:[22]

Stages	Pathways						
	I	II	III	IV	V	VI	VII
(1) $\xrightarrow{w_1}$ R	1	2	0	1	2	0	0
(2) M → R	1	0	2	1	0	2	0
(3) R + M → R + П	0	0	0	1	1	1	1
(4) 2R → chain termination	1	1	1	1	1	1	0

If the experimental relation $[M]^{exp}(t)$ is determined by a solution of the general direct problem with smaller dimensions, i.e.

$$\frac{d[M]}{dt} = -k_{eff}[M]; \quad [M](0) = [M]^0,$$

then the experimental data will be described by a kinetic model corresponding to pathway III:

$$\frac{d[M]}{dt} = -k_3[M]$$

and the model corresponding to cyclic pathway VII, where the concentration of active centres is determined by pathway II:

$$\frac{d[M]}{dt} = -\varkappa[M],$$

where $\varkappa = k_3(w_1/k_4)^{1/2}$.

An analogous situation has already been considered above for the case of a consecutive chemical reaction.[127] The existence of several special kinetic models, describing equally well the experimental data, has been demonstrated, for example, in two investigations,[26,114] while the existence of local minima in the functionals, in which the quality of the description of the experimental data is different, has been described in other studies.[20,115,132]. Thus the need arises for a procedure whereby the local minima could be sorted and which would make it possible to find a unique solution to the problem of the identification of the reaction mechanism or which would demonstrate the non-unique nature of the solution.

As can be seen from the examples presented, local minima arise in the region of the rate constants space corresponding to different special kinetic models.[21] The hypothesis that, in the region where a particular kinetic type of reaction mechanism applies, local minima can exist enabled Pavlov and Brin[22] to reduce the problem of sorting the local minima to the problem of dividing the rate constant space into sections in which the system (1) has specific asymptotic properties. This creates the possibility of extending the approach, used in the selection of the possible process scheme,[13–15,26,50,102,131] to the problem of the identification of the kinetic type of reaction mechanism.[22,80] Thus the solution of the problem at this level (when the hypotheses $П_1$–$П_3$ are known) is determined by the following procedure:[80]

(1) The formal treatment of the qualitative data concerning the process in the form of a system of control requirements common to all the alternative hypothetical mechanisms.

(2) The formulation of hypotheses and specification of a system of special control requirements distinguishing one hypothesis from another (taking into account the possible change in the reaction regime).

(3) The selection for each hypothesis of the initial values of the rate constant ensuring the satisfaction of the control requirements (general and special) and a parametric test of the adequacy of the corresponding mathematical models.

(4) Statistical analysis of the results of tests of each hypothesis.

(5) Logical design of a discriminating experiment.

(6) The representation of the results of the solution of the problem.

Fairly extensive experience has now accumulated in the solution of problems in terms of such formulation. For example, this procedure has been used to select the most probable mechanism of the radiation-initiated isotope exchange between deuterium and the hydroxy-groups of silica gel,[26] to investigate the mechanism of the formation of methane in the pyrolysis of ethane,[133] to establish a possible mechanism of the oxidation of anthrahydroquinone by molecular oxygen,[122] to study the catalytic hydrogenation of phenol and the conversion of methane,[13] to model the kinetics of the liquid-phase oxidation of tetralin,[104] to identify the mechanism of the inhibited liquid-phase oxidation of hydrocarbons,[101,102] etc. In the main, hypothetical mechanisms differing in the set of elementary stages were considered in these investigations and the limiting transitions to systems of differential-algebraic equations were assumed to be known *a priori*.

The abundance of kinetic types of reaction mechanisms, which can be formally realised within the framework of a complex scheme, and the sometimes extremely large expenditure of computer time on the test of each hypothetical mechanism limit the scope of the approach. We shall list certain procedures which make it possible to overcome these difficulties and to facilitate and accelerate the solution.[22,80] Firstly, *a priori* information can be used to reduce the number of hypotheses considered. Secondly, it is possible to design and carry out an experiment whose aim is to compare qualitatively the principal observed kinetic features with the features obtained using various special kinetic models. For example, comparison of the experimental ratio of the initial rates of consumption of methylacrolein and the accumulation of methacrylic acid with the same ratio arising from different hypotheses about the reaction mechanism made it possible to eliminate a series of hypothesis from consideration.[80] Thirdly, one can design and carry out an experiment which makes possible the successive refining of the mechanism with increase of the amount of experimental material available. For example, this approach made it possible to analyse at each stage of the treatment not more than three hypothetical kinetic types of reaction mechanisms.[115]

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Thus, the study of converse problems can be recommended to experimenters as a method facilitating the complex procedure whereby one establishes the mechanisms of chemical reactions. By regarding the study of converse problems as a generalised kinetic approach to the construction of mathematical models, one can use such studies as a method for the investigation of the mechanisms of complex reactions.

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