CONSECUTIVE CHEMICAL REACTIONS

Mathematical Analysis and Development

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PREFACE TO THE ENGLISH EDITION

The present translation of this monograph is a most interesting addition to the English chemical literature. It provides, first, an introduction to the powerful methods of the operational calculus in the solution of complicated systems of linear differential equations. Second, it contains an extensive collection of the results of such analyses on a large number of general types of consecutive reaction systems. It also presents the necessary apparatus for the application of the Laplace-Carson transformation to the solution of the equations for kinetic systems which are not treated specifically in the monograph.

The editor has chosen to retain the word "original" for what is frequently called the "inverse transform" in the literature of integral transforms since it seems to convey better the operational concept in the particular application. In Chapter VII, the adjective "conditional" has been used to characterize the reduced time which arises when the conversion to relative rate constants is made.

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Stony Brook, N. Y.
April 1963

INTRODUCTION

Knowledge of changes in the composition of interacting components is essential for a scientifically sound interpretation of any chemical process.

Early studies on the kinetics of chemical reactions date back to the latter half of the 19th century. N. N. Beketov, a Russian scientist, laid the foundations of this branch of knowledge when he demonstrated that the direction of a chemical process depends on the concentrations of substances entering the reaction. He also provided experimental proof of the principle which was subsequently given a mathematical expression in the law of mass action.

A little later the Swedish scientists Guldberg and Waage established a quantitative relationship between the rate of reaction and the concentration of reactants, as well as the concentration ratio of interacting substances at equilibrium.

A mathematical expression of kinetic laws was given for the first time by Van't-Hoff.

The rapid growth of the vast chemical industry at the turn of the century called for a thorough understanding of kinetic regularity patterns. A method was needed for precalculating the chain of consecutive reactions which is the basis of any industrial process.

In 1906 Kaufler [1] proposed a mathematical solution of a two-stage consecutive-irreversible reaction. In the same year Rakovsky [2] published an extensive study on the mathematical analysis of consecutive reactions. After examining consecutive irreversible, reversible and reversible-consecutive reactions, he developed, apparently for the first time, a system of differential equations expressing the course of these reactions. One such system was given for a reversible reaction of *n* stages, the most complicated of all those listed above. Rakovsky solved a system of differential equations for a three-stage consecutive-irreversible reaction, as well as for a reversible-consecutive one of two stages. For the last type of reaction two variants were examined: 1) the first reaction irreversible, the second reversible, and conversely 2) the first reaction reversible, the second irreversible.

In the same year (1906) Grüner [3] calculated a consecutive-irreversible four-stage reaction. The same type of reaction in n stages was calculated by Abel [27].

A method for calculating a consecutive-irreversible n-stage reaction was described in a handbook on experimental physics published in 1928 [4]. A few cases of practical application in the field of radioactive decay were cited by way of illustration.

Some material on solving differential equations for consecutive-irreversible reactions of n stages was included in a textbook compiled by A. N. Murin some thirty years later [5].

In subsequent reports of a theoretical nature [6-8] nothing new was introduced, except that methods for solving differential equations were given in modified versions for various reactions.

In 1950 Yerofeyev, in his comprehensive study [6], used an integrating multiplier e^{-kt} to solve the differential equations for a consecutive irreversible reaction of n stages, with any number of initial reactants. To simplify the final expressions, Yerofeyev introduced the so-called kinetic determinants. He also derived a number of essential relationships governing this type of reaction.

In 1956 Westman and De Lury [7] proposed a specific notation system for the constant coefficients in the differential rate equations, based on solving the differential equations for individual cases of simple interaction. By use of this method, tentative expressions for concentrations can be written, without going through a proper integration of the differential equations.

In 1957 Plyusnin and Rodiguin [8] used an operator method, with the Laplace-Carson transformation, to solve the differential equations for consecutive-irreversible reactions.

Differential equations of the same type were also solved by an operator method using the Laplace transformation [9].

L. Gold, in a recently published report [10], derived kinetic equations for a complex parallel-consecutive reaction. He showed that his mathematical treatment can be applied in cases where the hydrogen atoms in a benzene ring have been replaced by substituents of any kind, with provision for the formation of all possible derivatives.

Simultaneously with the elaboration of the theory, the course of consecutive reactions was calculated for some practical cases arising in various fields of chemistry and physics.

Solutions were found for problems in radioactive decay [4, 5, 9], methylation of xylene [11, 12], ethylation of benzene [13], destructive hydrogenation of benzene [14], alkylation of benzene by olefins [15-20], etc.

The present monograph treats specifically the operator method as applied to the solution of the differential equations. A summary of relevant material based on previous studies is amplified by the new methods for analyzing and calculating complex consecutive reactions, etc., developed by N. M. Rodiguin at the Physics of Metals Institute, Academy of Sciences USSR.

The authors examine monomolecular consecutive-irreversible, reversible, reversible-consecutive, parallel-consecutive and parallel-consecutive reactions with cross links, as well as chain reactions. In most cases an unlimited number of stages has been considered, given various amounts and arrangements of initial reactants.

For certain reactions, the governing relationships are discussed. Conditions are analyzed under which the concentrations pass through a maximum. Concentration changes affecting intermediate products at the initial moment, and some other details, are noted.

The monograph goes on to describe a method for calculating the composition of products from rate constants and, conversely, a method for determining rate constants from the product composition. Practical examples are included.

The theoretical foundations and essential features of the operator method for solving differential equations are expounded, with a view to convenient reference, in Appendixes I and II. A table of transforms and originals is added.

The authors are indebted to Dr. Chem. Sci. V. G. Plyusnin and Cand. Chem. Sci. Ye. P. Babin for suggestions made with regard to alkylation of benzene by olefins.

CONTENTS

Chapter I

TYPES OF CHEMICAL REACTIONS

In relation to kinetics, *simple chemical reactions* are grouped on the basis of their molecularity, or of their order.

The molecularity of a reaction is defined as the number of molecules which interact simultaneously and which undergo chemical transformation. On this basis, mono-, bi- and ter-molecular reactions are distinguished. Higher molecularities are practically unknown.

The order of a chemical reaction is defined as the order of an equation expressing the dependence of reaction rate on the concentration of reactants. The order is numerically equal to the sum of the powers to which concentrations are raised in a given rate equation.

Reactions of the first, second and third order are known. Higher orders have never been observed. There are, furthermore, reactions of the zeroth order, the velocity of which does not vary with time. Occasionally the order of a reaction is expressed by a fractional number.

By way of illustration, we shall consider the equations for reactions of various orders in one component:

$$\text{first order} \quad \frac{dC}{dt} = k_1C;$$

$$\text{second order} \quad \frac{dC}{dt} = k_2C^2;$$

$$n\text{th order} \quad \frac{dC}{dt} = k_nC^n.$$

It should be noted that the order of a reaction does not always coincide with its molecularity.*

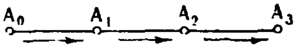
---

* For instance, when an ester is saponified with water in a dilute aqueous solution, the change in water concentration is negligible and the rate of reaction depends only on the change of ester concentration. As a result, reaction kinetics are described in this case by an equation of the first order, even though the reaction is a bimolecular one.

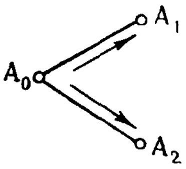
Complex chemical reactions are defined kinetically as systems of two or more simple reactions which are in some way interconnected. In developing a theory of complex reactions it is assumed that several simple reactions proceed simultaneously within a given system, and that each one of them proceeds independently of the others. It follows that the general kinetic equations for simple reactions are applicable to this case.

Complex chemical reactions are divided, according to the way in which the component simple reactions are interconnected, into consecutive, parallel, reversible, conjugated and mixed.

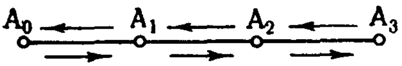
Consecutive chemical reactions are those in which the initial substance and all the intermediate products can react in one direction only:



Parallel chemical reactions are those in which the initial substance reacts to produce two different substances simultaneously:



Reversible reactions are those in which two substances entering a single simple consecutive chain reaction interact in both forward and backward directions:

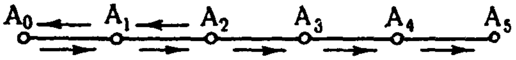


Conjugated reactions are two simultaneous reactions in which only one substance A_0 is common to both:

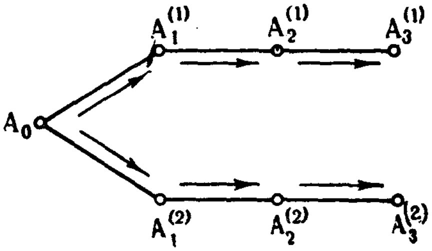
$$A_0 + A_1 = A_3;$$
$$A_0 + A_2 = A_4.$$

The first (or second) reaction will not take place unless A_0 and A_1 (or A_0 and A_2) are used as initial substances. All three initial substances A_0, A_1 and A_2 must be present in the reaction mass in order for both reactions to take place concurrently. In other words, substance A_1, while reacting with A_2, seems to impart some of its reactivity to A_0, or vice versa. Such a reactivity transfer from one reaction to another is called *chemical induction.*

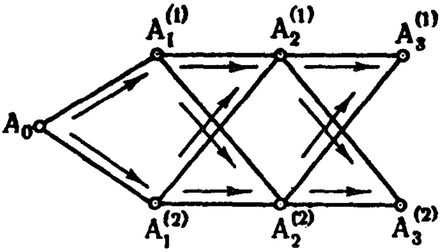
Another broad group of mixed reactions represent the case in which two or more reactions, each of a different type, occur simultaneously. The *reversible-consecutive* reactions, to name one common type, combine some characteristics of consecutive-irreversible and reversible reactions. Shown below is a reversible-consecutive reaction consisting of five simple reactions, two of them reversible, and three of the consecutive-irreversible type:



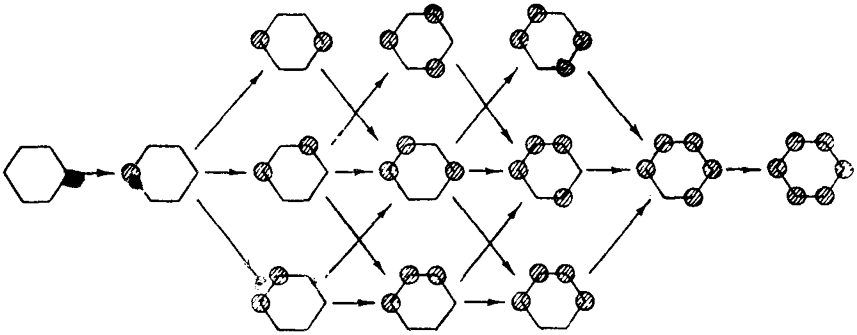
Parallel-consecutive reactions also belong to the mixed type. These have the characteristics of both parallel and consecutive reactions. The reaction scheme shown below comprises two parallel chains, each composed of three simple reactions:



A parallel-consecutive reaction becomes complex when substances that belong to different chains interact as shown below:



A *complex parallel-consecutive* reaction is illustrated by the following scheme, which represents the complete stepwise substitution of a benzene ring:



This reaction is theoretically possible in the case of benzene alkylation.

If the initial substance and each intermediate reaction product interact simultaneously with different substances and in different directions, such processes are known as chain reactions (see Chapter VI). Other types of chain reactions are described in detail by Semenov, Akulov and others [21, 22].

The course of the process is determined not only by the type of resultant reaction but by the rate constants of the component reactions as well.

According to a concept developed by Academician Semenov [23], the rate constant of a reaction is a number expressing the reactivity of a molecule when attacked by some radical along a chemical bond.

The rate constant of a monomolecular reaction is determined from the equation

$$k_1 = a_1 e^{-E_1/RT} C,$$

while for a bimolecular reaction the corresponding expression is

$$k_2 = a_2 e^{-E_2/RT} C_1 C_2,$$

where E_1 is the activation energy of the elementary reaction and indicates the least amount of energy necessary to trigger a reaction within the system (i.e., the energy of one molecule or one radical in a monomolecular process, or the sum of energies of two interacting particles in a bimolecular process); and a_1 represents the vibration frequency of a ruptured bond. For most monomolecular reactions its magnitude is of the order 10^{13} sec^{-1}.

The preexponential factor a_2 in a bimolecular reaction is often numerically close to the number of collisions z between radicals and molecules. Its magnitude is therefore of the order 10^{-10} cm^3/sec or 10^{14} $cm^3/sec \cdot mole$ (depending on the units in which the concentrations are expressed).

In reality, however, not every collision of a radical with a molecule leads to a reaction, even if the energy of the colliding particles is sufficient to overcome the activation barrier. Hence $a_2 = fz$, where f is the so-called steric multiplier (the numerical value of which is usually less than unity). In many substitution reactions f ranges from 0.1 to 1. Some recently published data demonstrate that the value of f is of the order 10^{-3} to 10^{-4} for substitution reactions involving hydrocarbon radicals and hydrogen atoms in paraffins. The question of the numerical values of the steric factors in such reactions is still somewhat of a problem.

In the present study a method is proposed for calculating the concentrations of all reactants from the given rate constants. At the same time, probing into the essential nature of rate constants lies outside the scope of this work. Such problems have been treated most comprehensively by N. N. Semenov [23].

Chapter II

CONSECUTIVE–IRREVERSIBLE REACTIONS

In a consecutive-irreversible reaction the initial substance and all the intermediate products react in one direction only.

The total number of substances participating in the reaction may vary within wide limits, from $n=2$ to $n=\infty$, and the number of initial substances from $m=1$ to $m=\infty$. The initial substances may be designated in any desired manner from A_0 to A_m with numbers assigned either in direct succession or at any specified interval. Thus, for $m=9$, the initial substances may be designated as A_0, A_2, A_5, A_9.

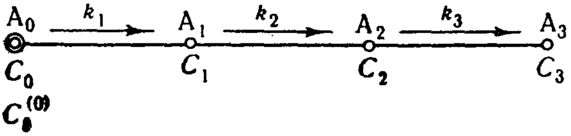
Consecutive-irreversible reactions are conveniently classified according to the number of stages or the number of initial substances.

CONSECUTIVE-IRREVERSIBLE THREE-STAGE REACTION WITH A SINGLE INITIAL SUBSTANCE A_0

Let us examine a consecutive-irreversible reaction in which four substances participate: A_0, A_1, A_2 and A_3. The initial substance A_0 has an initial concentration $C_0^{(0)}$. The reagent B which effects the reaction has a concentration Z. This value is assumed to remain constant through all stages of the reaction (i.e., each reaction is assumed to be first order).

The reaction consists of three simple reactions. In the first, substance A_0 interacts with substance B, forming substance A_1; in the second, A_1 is converted to A_2; and in the third, A_2 is transformed into A_3. The specific rate constants for these reactions are, respectively, k'_1, k'_2 and k'_3.

The course of the reactions is shown in the scheme below, which also indicates the rate constants:



Our problem is to determine the concentrations of the reaction products at any moment in the course of the process. Let the substances participating in the reaction (A_0, A_1, A_2 and A_3) have at time t the respective concentrations C_0, C_1, C_2 and C_3.*

Considering that these simple reactions follow one another in direct succession, the concentration of any substance which has reacted by the time t can be expressed by one of the following equations:

for substance A_0 . . . . $C_0^{(0)} - C_0$;
" " A_1 . . . . $C_0^{(0)} - C_0 - C_1$;
" " A_2 . . . . $C_0^{(0)} - C_0 - C_1 - C_2$;
" " A_3 . . . . $C_0^{(0)} - C_0 - C_1 - C_2 - C_3 = 0$.

Assuming the rate at which each substance is consumed to be directly proportional to its concentration, we can write the following set of equations:

$$\left.\begin{aligned}
\frac{d\left(C_0^{(0)} - C_0\right)}{dt} &= k_1' C_0 Z;\\
\frac{d\left(C_0^{(0)} - C_0 - C_1\right)}{dt} &= k_2' C_1 Z;\\
\frac{d\left(C_0^{(0)} - C_0 - C_1 - C_2\right)}{dt} &= k_3 C_2 Z;\\
\frac{d\left(C_0^{(0)} - C_0 - C_1 - C_2 - C_3\right)}{dt} &= 0.
\end{aligned}\right| \tag{II.1}$$

After a few simple rearrangements, we obtain

$$\left.\begin{aligned}
\frac{dC_0}{dt} &= - k_1' C_0 Z;\\
\frac{dC_1}{dt} &= k_1' C_0 Z - k_2' C_1 Z;\\
\frac{dC_2}{dt} &= k_2' C_1 Z_1 - k_3' C_2 Z;\\
\frac{dC_3}{dt} &= k_3' C_2 Z.
\end{aligned}\right| \tag{II.2}$$

---

*For this reaction, as well as for those that follow, the symbols are assigned according to the same rule: Substances, concentrations and rate constants are designated by A, C and k, respectively. The subscript on A denotes an ordinal number, which represents the consecutive order in which the substances are obtained. The subscript on C has the same meaning as that for A. Initial concentration of the initial substance is denoted by a superscript (0). The subscript on k indicates the ordinal number of the reaction stage.

With a view to simplification, the constant Z is introduced into the values of the rate constants. We now have

$$\left.\begin{aligned}
\frac{dC_0}{dt} &= -k_1C_0;\\
\frac{dC_1}{dt} &= k_1C_0 - k_2C_1;\\
\frac{dC_2}{dt} &= k_2C_1 - k_3C_2;\\
\frac{dC_3}{dt} &= k_3C_2.
\end{aligned}\right\} \qquad (II.3)$$

Here $$k_1 = k_1' Z;\ k_2 = k_2' Z;\ k_3 = k_3' Z; \qquad (II.4)$$

k_1, k_2 and k_3 are the conventional rate constants.

The system of linear differential equations we have obtained, as well as all other systems of this type that follow, will be solved by the operator method. The essential features and theoretical basis of this method for solving differential equations are discussed in Appendix I.

Let the unknown functions in the system of differential equations (II.3) be replaced by transformed ones, i.e., by their transforms. Let us further replace the differentiation procedure by a multiplication procedure, in which operator $P = \frac{d}{dt}$ is the multiplier. We must keep in mind that the initial concentration of substance A_0 is $C_0^{(0)}$, while the initial concentration of each of the other substances is zero:

$$\left.\begin{aligned}
PC_0 - PC_0^{(0)} &= -k_1C_0;\\
PC_1 &= k_1C_0 - k_2C_1;\\
PC_2 &= k_2C_1 - k_3C_2;\\
PC_3 &= k_3C_2.
\end{aligned}\right\} \qquad (II.5)$$

In these equations the transforms of the unknown functions are designated by the same letter as their originals.

Solving equations (II.5) in succession as ordinary algebraic expressions, we find

$$\left.\begin{aligned}
C_0 &= \frac{PC_0^{(0)}}{P + k_1}\\
C_1 &= \frac{k_1PC_0^{(0)}}{(P + k_1)(P + k_2)}
\end{aligned}\right\} \qquad (II.6)$$