# A GRAPHICAL METHOD FOR DERIVING KINETIC EQUATIONS OF COMPLEX REACTIONS\

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## Abstract

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### PHYSICAL CHEMISTRY

**M. I. TEMKIN**

# A GRAPHICAL METHOD FOR DERIVING KINETIC EQUATIONS OF COMPLEX REACTIONS*

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Stationary (or quasi-stationary) reactions obey the equation (1,2)

$$r^{(1)}\left(\frac{\nu_{s_1}^{(1)}}{r_{s_1}}+\frac{r_{-s_1}\nu_{s_2}^{(1)}}{r_{s_1}r_{s_2}}+\frac{r_{-s_1}r_{-s_2}\nu_{s_3}^{(1)}}{r_{s_1}r_{s_2}r_{s_3}}+\ldots\right)+$$
$$+r^{(2)}\left(\frac{\nu_{s_1}^{(2)}}{r_{s_1}}+\frac{r_{-s_1}\nu_{s_2}^{(2)}}{r_{s_1}r_{s_2}}+\frac{r_{-s_1}r_{-s_2}\nu_{s_3}^{(2)}}{r_{s_1}r_{s_2}r_{s_3}}+\ldots\right)+\ldots=$$
$$=1-\frac{r_{-s_1}r_{-s_2}r_{-s_3}\cdots}{r_{s_1}r_{s_2}r_{s_3}}, \tag{1}$$

where $r^{(1)}, r^{(2)}, \ldots$ are the reaction rates along the basic routes; $r_{s_1}$ and $r_{-s_1}$ are the rates of the forward and reverse elementary reactions which together constitute stage $s_1$; $\nu_{s_1}^{(1)}$ is the stoichiometric number of stage $s_1$ along route (1), etc. The stages are numbered $s_1, s_2, s_3 \ldots$, and not $1, 2, 3 \ldots$, in order to show that the order of the stages in (1) may be arbitrary. If all or some of the reaction stages are reversible, equation (1) can substantially facilitate the determination of kinetic equations.

We shall restrict ourselves to considering such stationary reactions in which the chemical equation of each stage contains, both on the left- and on the right-hand side, no more than one molecule of intermediate substances (3). In this case the rates of the stages depend linearly on the concentrations of the intermediate substances. Reaction mechanisms satisfying the indicated restriction will be called linear.

If there is no intermediate substance on the left- or right-hand side of the chemical equation of a stage, we shall assume that its absence is compensated by a “zero-substance.” This makes it possible to associate a graph (multigraph) with

Fig. 1

Figure 1: Fig. 1

any linear reaction mechanism (4). The vertices of the graph represent intermediate substances or the zero-substance. A stage in which two intermediate substances, or an intermediate substance and the zero-substance, participate is represented by an edge connecting the corresponding vertices (elementary reactions correspond to arcs of the graph). We take one and the same zero-substance for all stages of one connected component. The concentration or (for nonideal systems) the activity of the zero-substance is always taken to be equal to 1, so that the introduction of the zero-substance is not reflected in the expressions for the rates of the elementary reactions.

As an example, Fig. 1 gives the graph of a chain reaction:

1) $A_1 \rightleftarrows X_1 + B_1$;

2) $X_1 + A_2 \rightleftarrows X_2 + B_2$;

3) $X_2 + A_3 \rightleftarrows X_1 + B_3$;

4) $X_2 + A_4 \rightarrow B_4$

($A_1, A_2, \ldots$ are the initial substances; $B_1, B_2, \ldots$ are products; $X_1$ and $X_2$ are intermediate substances). The vertices are depicted by circles, the edges by lines. The empty vertex represents the zero-substance. At the edges are indi- the numbers of the steps and their orientation are specified (which, in the case of reversible steps, is arbitrary and is given by the notation of the mechanism). The irreversibility of step 4) is shown by the arrow on the line.

The cycles of such a graph correspond to reaction routes; the stoichiometric number of any step is equal to the difference between the numbers of traversals of the corresponding edge in the positive and negative directions when going around the cycle. It is easy to see that, when the chemical equations of the steps multiplied by the stoichiometric numbers determined in the indicated way are summed, the intermediates cancel out. The cyclomatic number of the graph (the largest number of independent cycles) (4) is, in the language of chemical kinetics, the number of basic routes.

**Fig. 1**

A step corresponding to a loop or to an edge leading to a pendant vertex has stoichiometric numbers 0 for all routes and, consequently, is an equilibrium step. Such steps may be taken into account by equilibrium equations, and the edges

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representing them may be discarded. If, in the chain-reaction mechanism given above, step 4) were absent, the empty vertex (Fig. 1) would be pendant; after discarding step 1), the role of the empty vertex passes to vertex $X_1$, adjacent to the empty one, because the concentration $X_1$ is determined by equilibrium 1).

Usually the reaction mechanism satisfies the requirements of the Pontryagin-Kuratowski theorem ($^4$) and therefore can be represented in the plane without intersections of edges (a planar topological graph). In this case the boundaries of the finite faces determine a basis of independent routes. For example, the two finite faces of Fig. 1, for the directions of traversal shown in the figure, correspond to 2 basic routes: (1) –stoichiometric numbers $0, 1, 1, 0$, chemical equation $A_2 + A_3 = B_2 + B_3$ (the main reaction); (2) –stoichiometric numbers $1, 1, 0, 1$, chemical equation $A_1 + A_2 + A_4 = B_1 + B_2 + B_4$ (consumption of inhibitor $A_4$).

When the 0-substance is absent (catalytic processes), the concentrations of intermediates are not independent but are connected by at least one balance equation. For heterogeneous catalytic processes the balance equation expresses the requirement that the sum of the surface coverages by the various substances and the fraction of free surface be equal to 1. If the reaction proceeds on several types of surface sites without surface migration, each type of site has its own connected component of the graph and its own balance equation. Each connected component of the reaction-mechanism graph may be considered independently of the others.

We proceed to finding the kinetic equations with the aid of equation (1). First let us consider mechanisms in which at least one step is irreversible; in this case

$$r_{-s_1} r_{-s_2} r_{-s_3} \ldots / r_{s_1} r_{s_2} r_{s_3} \ldots = 0.$$

For substitution into (1) we use a sequence of steps corresponding to a simple chain (i.e., a chain without repeated passages along edges), which ends by passage in the positive direction of the edge corresponding to the irreversible step. Then in (1) the concentrations of all intermediates except the initial one cancel. If the simple chain begins with the 0-substance, the concentrations of all intermediates cancel. Using as many such chains as there are basic routes, we obtain a system of linear equations for determining $\gamma^{(1)}, \gamma^{(2)}$, etc.

For example, in the case of the reaction in Fig. 1 we use the following chains. First chain: 0-substance, step 1), substance $X_1$, step 2), substance $X_2$, step 4), i.e. $s_1 = 1, s_2 = 2, s_3 = 4$. Second chain: 0-substance, step 1), substance $X_1$, step 3) in the reverse direction, substance $X_2$, step 4), i.e. $s_1 = 1,\ s_2 = -3,\ s_3 = 4$. Since $r_1 = k_1[A_1]$ ($k_1$ is the rate constant, $[A_1]$ is the concentration of $A_1$), $r_{-1} = k_{-1}[X_1][B_1]$, etc., we obtain the system

equations

$$r^{(1)} \frac{k_{-1}[\mathrm{B}_1]}{k_1[\mathrm{A}_1]\, k_2[\mathrm{A}_2]} + r^{(2)} \left( \frac{1}{k_1[\mathrm{A}_1]} + \frac{k_{-1}[\mathrm{B}_1]}{k_1[\mathrm{A}_1]\, k_2[\mathrm{A}_2]} + \frac{k_{-1}[\mathrm{B}_1]\, k_{-2}[\mathrm{B}_2]}{k_1[\mathrm{A}_1]\, k_2[\mathrm{A}_2]\, k_4[\mathrm{A}_4]} \right) = 1,$$

Fig. 2

Figure 2: Fig. 2

$$r^{(1)}\frac{k_{-1}[\mathrm{B}_1]}{k_1[\mathrm{A}_1]\,k_{-3}[\mathrm{B}_3]}+r^{(2)}\left(\frac{1}{k_1[\mathrm{A}_1]}+\frac{k_{-1}[\mathrm{B}_1]\,k_3[\mathrm{A}_3]}{k_1[\mathrm{A}_1]\,k_{-3}[\mathrm{B}_3]\,k_4[\mathrm{A}_4]}\right)=1, \qquad (2)$$

from which we determine $r^{(1)}$ and $r^{(2)}$.

Simple chains that begin with an intermediate substance and end with an irreversible stage make it possible to express the concentration of this substance through the concentrations of the initial substances and products and the rates along the basis routes.

In reactions without a 0-substance, the expressions for the concentrations of intermediate substances found in this way are substituted into the balance equation, and thereby the concentrations of the intermediate substances are eliminated (2). If all stages of the reaction are reversible and the degrees of all vertices of the graph are even (the degree of a vertex is the number of edges incident to it), then the kinetic equations can be obtained by the method described above with the aid of Eulerian cycles (i.e., cycles including all stages once). In this case the concentrations of all intermediate substances in the term $r_{-s_1}r_{-s_2}r_{-s_3}\ldots/r_{s_1}r_{s_2}r_{s_3}\ldots$ cancel. A reversible reaction whose graph contains vertices of odd degree and, consequently, does not admit Eulerian cycles requires a special device.

**Fig. 2**

We shall assume that the graph of a reversible reaction is connected and contains no hanging vertices or isthmuses. Several edges, for example 3 (Fig. 2), converge to an empty vertex. Suppose that a point whose motion represents the reaction leaves this vertex along edge 1), traverses some path in the graph, and returns to the initial vertex; this corresponds to a single run of the reaction along the corresponding route; such a run can be represented as a linear combination of runs along the basis routes. If stages 2) and 3) are made irreversible, permitting motion only toward the empty vertex, as shown in Fig. 2 I, this will not affect the motion of the point that has left along edge 1). In exactly the same way, if the point leaves along edge 2) or 3), stages 1) and 3) or 1) and 2), respectively, may be regarded as irreversible (Fig. 2 II and 2 III). The foregoing consideration exhausts all possible variants of the motion of the representative point.

Let $r^{(p)}$ denote the rate of reaction along the basis route $p$, and let $r_I^{(p)}$, $r_{II}^{(p)}$, $r_{III}^{(p)}, \ldots$ denote the rates along the corresponding route for the imaginary irreversible reactions whose mechanism fully coincides with the one under consideration, except that all stages leading to the empty vertex, except one, are taken to be irreversible. Then, since the concentration of the 0-substance is always equal to 1,

$$r^{(p)} = r_I^{(p)} + r_{II}^{(p)} + r_{III}^{(p)} + \dots \tag{3}$$

An analogous equation is also valid for the concentrations of intermediate substances:

$$[\mathrm{X}_j] = [\mathrm{X}_j]_I + [\mathrm{X}_j]_{II} + [\mathrm{X}_j]_{III} + \dots, \tag{4}$$

where $[\mathrm{X}_j]$ is the concentration of the intermediate substance $\mathrm{X}_j$ in the reversible reaction, and $[\mathrm{X}_j]_I$, etc., are the concentrations of this substance in the imaginary irreversible reactions characterized above, which in what follows we shall call irreversible component reactions.

Thus, the problem of the kinetics of a reversible reaction is reduced to problems of the kinetics of irreversible reactions. The latter, in the case of a linear mechanism, can be solved by the method described above. If there is no empty vertex, then a vertex corresponding to an intermediate substance whose concentration is to be determined for substitution into the balance equation may serve for decomposing the reaction into irreversible terms.

The concept of the reaction rate in the forward and reverse directions (1,2) is a special case of the relations discussed. This concept applies to reactions with one independent route; in such reactions the degree of each vertex is equal to 2, and, consequently, the number of irreversible terms is always equal to 2. The reaction rate in the forward direction is $r_+ = r_I$, and the reaction rate in the reverse direction is $r_- = -r_{\mathrm{II}}$.

Sometimes the rates of a directed term of a reaction along the basic routes can be made accessible to measurement by means of labeled atoms.

Physicochemical Institute
named after L. Ya. Karpov

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