ALGORITHM FOR FORMAL KINETICS OF CATALYTIC REACTIONS; APPLICATIONS TO TWO STEPS CATALYTIC REACTIONS

E. Segal[*]

abstract: The author presents some elements of graph theory applied in writing rate equations of homogeneous catalytic reactions, particularly reactions used in analytical chemistry. Actually the kinetic graph technique and the, already classical, quasi steady state approximation (QSSA) are alternative procedures which if correctly applied should lead to similar results. Thus, for a given catalytic system, one should use the less cumbersome technique which leads without loss of rigour and with minimum effort of calculation to the searched rate equation. The paper could be considered as a message of the author, who happens to be a professor of chemical kinetics, to the analytical chemists interested in one of the most fruitful applications of its teaching field in analytical chemistry.

Generalities

One of the most spectacular applications of chemical kinetics, particularly of the kinetics of homogeneous reactions, in analytical chemistry was the setting up of the kinetic methods of analysis. According toYatzimirskii [1] the kinetic methods of analytical chemistry exhibit one of the highest sensitivities. The lower theoretical limit of these methods is 10^{-17} mole/l [2]. These circumstances might be considered among the reasons for nowaday there were developed kinetic methods to determine more than 70 elements of the periodic system [3].

In order to determine microamounts of elements by means of the kinetic methods, more often redox catalytic homogeneos reactions are used [4]. As indicators various compounds which can be easy either oxidized or reduced in presence of traces of elements which act as catalysts can be used.Actually in the kinetic methods of analysis one defines an indicator compound as the compound whose change in concentration in time is followed in order to evaluate the reaction rate. As an example of an indicator reaction we mention the following one:

$$ClO_3^- + 6I^- + 6H^+ = Cl^- + 3J_2 + 3H_2O$$
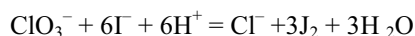
[*] Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bd. Regina Elisabeta No. 4-12, Bucharest, Roumania
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catalysed by Y, Re, Ru, Os, whose indicator compound is the molecular iodine. The increase of iodine concentration in solution is used to determine the reaction rate [5].

Other kinds of reactions like those with generation of polarographic catalytic curents,isotopic exchange reactions, substitutions in the inner sphere of coordination compounds,enzyme reactions and induced reactions are mentioned as being used in the kinetic methods of analysis too [5].

Concerning the kinetics of catalytic reactions, in this lecture I am going to present an algorithm based on graphs for writing rate equations. Although general, the algorithm is going to be applied to catalytic reactions of interest in analytical chemistry. Actually this algorithm is an alternative to the QSSA applied to the formal kinetic treatment of the same class of catalytic reactions.

The graph theory originates in the works of Euler [6,7], Kirchoff [6,8] and Cayley [6,9] who aimed respectively to solve the famous problem of Königsberg bridges, to calculate the current intensity in electrical networks as well as to enumerate the constitutive isomers of the alcanes.

Used at its beginning for recreative purposes, the graph theory found its applications only after 1900. Among the beneficial fields one has to mention: electrical engineering, automatics, city planning and chemistry [6,10].

Christiansen [11] can be considered as a precursor in using graphs in chemical kinetics. He applied graphical schemes not yet comprised in the framework of the graph theory, in order to describe kinetically complex noncatalytic and catalytic reactions.

The first application of the graph theory in chemical kinetics in order to describe the kinetics of fermentative reactions is due to King and Altman [12]. Volkenshtein and Goldshtein extended and applied the graph theory to the kinetic investigation of enzyme reactions [13]. Besides the extension of the graph theory to the kinetic analysis of multiroute catalytic reactions [14,15], Temkin suggested a procedure to derive rate equations for noncatalyric reactions [16]. Snagovskii and Avetisov [17] used graphs in order to describe kinetically multiroute reactions which occur on nonuniform surfaces. The applicationof the graph theory to the kinetics of heterogeneous catalytic reactions as treated in the book of Snagovskii and Ostrovskii[18]should be mentioned too. A review article dedicated to the use of graphs in the kinetics of homogeneous as well as enzyme reactions is due to Yatsimirskii [10]. One has equally to mention Kiperman`s excellent book [19] dedicated to the kinetics of heterogeneous catalytic reactions. Three relatively recent contributions in the field, namely the works of Petrov [20], Temkin et al [21] and of the author of this article [22], I appreciate as being worth mentioning.

As far as some fundamentals on graphs needed for application in chemical kinetics, the author sends the interested readers to some literature sources [1,21÷25]. In this article we should limit only to few definitions strictly necessary for the understanding of the kinetic applications.

Definitions

Graph.	Graphical representation of a finite set of elements as well as the connexions between them. A graph G(X,Y) can be defined as a manifold consisting of two subsets :a nonzero subset, X, whose elementa are called vertices, and a subset, Y, whose elements are called edges.
Directed graph.	A graph containing drected (oriented) edges.
Multiple edge.	One from the several edges connecting two vertices.
Degree of a vertex.	Number of edges converging at a vertex.
Node.	Vertex with degree higher than two.
Branche.	Line joining two nodes.
Chain.	A line which crosses the same vertex several times and which passes through each edge only once.
Cicuit.	Chain which begins and ends at the same point.
Elementary chain.	A line which passes through the vertices of the graph(not necessary all the vertices) only once.
Route of the graph.	An alternative succession of vertices and edges connecting the first and the last vertices.
Connected graph.	A graph in which any vertex is connected to any other vertex through an elementary chain.
Tree.	Connected graph witout circuits.
Spanning (maximal) tree.	Tree which consists of all the vertices of a graph connected with arcs.
Cyclomatic number (υ).	The minimum number of edges which have to be removed from a connected graph in order to turn into a tree.

$$\upsilon = p - b + 1 \tag{1}$$

where p is the number of edges and b is the number of verices. The cyclomatic number equals the number of independent circuits (routes).

The extent of the graph.	The product of edge sizes in the graph.
The extent of the cycle.	The product of edge sizes in the circuit.
Basis.	Any vertex of the graph considered as initial.
Basic tree.	Chain passing through the vertices toward the basis and with the end in the basis.
Magnitude of the graph's route.	The product of successive edges (multiple edges in the given direction should be added)
Magnitude of the tree.	The product of the constitutive edges.

Determinant of the basis. The totality of all the possible trees directed to the basis and crossing all the vertices. This is obtained by adding the multiple edges directed toward the basis and by multiplying the successive ones.

Algorithm for reaction rate calculation

In the following, monoroute catalytic reactions with linear mechanism (a linear mechanism consists in linear elementary steps characterized by only one active center as reactant) are going to be considered. To a given mechanism one associates a graph with the active centers in the vertices and with the edges labelled with the elementary steps weights (frequencies). The frequency of the elementary step, ω, is defined as the ratio between the rate of the elementary step and the concentration of the active center attending it.

Vokenshtein and Goldshtein [13] derived the following relation between the concentrations of active centers attending steps i and j, X_i and X_j, and the basic determinants corresponding to the vertices of X_i and X_j, D_i and D_j.

$$\frac{X_i}{X_j} = \frac{D_i}{D_j} \tag{2}$$

whence it is easy to obtain:

$$\frac{X_j}{\sum X_i} = \frac{D_j}{\sum D_i} \tag{3}$$

Relation (3) was derived using a rule from electrotechnics known as Mason's rule [26,27].

In the kinetic calculations for homogeneous catalytic reactions one considers that the total cocentration of the active centers equals tne concentration of the catalyst i.e., .Under such conditions relation (3) turns into:

$$X_j = \frac{D_j}{\sum D_i} c_k \tag{4}$$

Taking into account that the rate of a stage (two reversible elementary steps) is given by the difference:

$$r = r_s - r_{-s} \tag{5}$$

as well as the obvious relations:

$$r_s = \omega_s X_s$$

where ω_s is the frequency of the step s, the rate (5) becomes:

$$r = \omega_s X_s - \omega_{-s} X_{-s} \tag{6}$$

or expressing X_S and X_{-S} taking into account relation (4), it follows that:

$$r = \left(\omega_s \frac{D_s}{\sum D_j} - \omega_{-s} \frac{D_{-s}}{\sum D_j} \right) c_k \qquad (7)$$

This is the searched formula for the calculation of the reaction rate.

Taking into account these considerations, the procedure to derive rate equations for monoroute homogeneous catalytic reactions comprises the following steps:

1. Write the reaction sequence consisting in linear steps or stages.

2. Draw the representative graph.

3. Calculate the determinants of bases corresponding to the vertices of the graph.

4. Apply formula (7) at least for one stage of the sequence in order to obtain the rate equation.

People less familiar with kinetic graphs should check the result by calculating in the same way the reaction rate for other stages or steps. Obviously the same rate equation should be obtained.

Examples

Once the algorithm is known, we are going to show how the chemist involved in kinetic procedures of analysis can relatively easy write rate equations by means of graphs.

Two step reactions .Among the most simple reactions which can be treated formal-kinetically by help of graphs one has to mention the two step homogeneous catalytic reactions. The results obtained by means of this procedure support an easy comparison with those obtained by applying the QSSA or by a treatment which suppose an equilibrium followed by a rate determining step. Two step catalytic reactions are important by themselves, many catalytic reactions occurring according to such a simple mechanism. Besides it can be demonstrated that the kinetic treatment of more complicated multistep reactions can be reduced, under given conditions, to the kinetic treatment of two step reactions [28].

In Table 1, rate equations obtained for the two step reactions, A + B = AB and AB = A + B, by means of graphs, by using the QSSA and by means of the equilibrium followed by a rate determining step procedure(the last one was for reversible first stages) are compared [29]. According to the recommendations from the previous section we give in column 1 the two step mechanism, the representative graph in column 3, the basic determinants in column 4 and the rate equations in column 5.These could be easily be compared with the so called classical rate equations(column 2) obtained by means either of an equilibrium stage followed by a rate determining step (the first two lines of the tables) or using the QSSA approximation. By looking at the rate equations one can notice that if the second step is considered as rate determining the classical procedures and that based on the graph theory lead to identical results. Thus, the graph treatment is a relatively simple alternative to the classical ones and sometimes is preferable to them due to its simplicity.

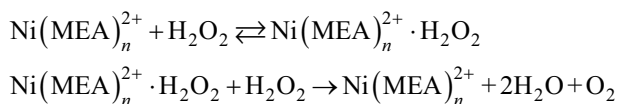**Table 1. Rate equations obtained by classical procedures and by means of graphs**

$$A + B \longrightarrow AB$$

Two-step Sequence	Classical rate Equation	Representative Graph	Basic Determinants	Rate equation obtained by means of graphs
$A + K \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AK^*$ $AK^* + B \xrightarrow{k_2} K + AB$	$r = \dfrac{k_1 k_2 C_A C_B}{k_{-1} + k_1 C_A} C_K$		$D_K = \omega_{-1} + \omega_2$ $D_{AK} = \omega_1$	$r = \dfrac{k_1 k_2 C_A C_B}{k_{-1} + k_1 C_A + k_2 C_B} C_K$
$A + B + K \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ABK^*$ $ABK^* \xrightarrow{k_2} K + AB$	$r = \dfrac{k_1 k_2 C_A C_B}{k_{-1} + k_1 C_A C_B} C_K$		$D_K = \omega_{-1} + \omega_2$ $D_{ABK^*} = \omega_1$	$r = \dfrac{k_1 k_2 C_A C_B}{k_1 C_A + k_{-1} + k_2} C_K$
$A + K \xrightarrow{k_1} AK^*$ $AK^* + B \xrightarrow{k_2} K + AB$	$r = \dfrac{k_1 k_2 C_A C_B}{k_1 C_A + k_2 C_B} C_K$		$D_K = \omega_2$ $D_{AK^*} = \omega_1$	$r = \dfrac{k_1 k_2 C_A C_B}{k_1 C_A + k_2 C_B} C_K$
$A + B + K \xrightarrow{k_1} ABK^*$ $ABK^* \xrightarrow{k_2} K + AB$	$r = \dfrac{k_1 k_2 C_A C_B}{k_1 C_A C_B + k_2} C_K$		$D_K = \omega_2$ $D_{ABK^*} = \omega_1$	$r = \dfrac{k_1 k_2 C_A C_B}{k_1 C_A C_B + k_2} C_K$

Table 1. Continued.

$$AB \longrightarrow A + B$$

Two-step Sequence	Classical rate Equation	Representative Graph	Basic Determinants	Rate equation obtained by means of graphs
$AB + K \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AK^* + B$ $AK^* \overset{k_2}{\longrightarrow} K + A$	$r = \dfrac{k_1 k_2 C_{AB}}{k_{-1} C_B + k_1 C_{AB}} C_K$	K ⇄ AK* (ω_1, ω_{-1}, ω_2)	$D_K = \omega_{-1} + \omega_2$ $D_{AK} = \omega_1$	$r = \dfrac{k_1 k_2 C_{AB}}{k_1 C_{AB} + k_{-1} C_B + k_2} C_K$
$AB + K \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ABK^*$ $ABK^* \overset{k_2}{\longrightarrow} K + A + B$	$r = \dfrac{k_1 k_2 C_{AB}}{k_{-1} + k_1 C_{AB}} C_K$	K ⇄ ABK* (ω_1, ω_{-1}, ω_2)	$D_K = \omega_{-1} + \omega_2$ $D_{ABK^*} = \omega_1$	$r = \dfrac{k_1 k_2 C_{AB}}{k_1 C_{AB} + k_{-1} + k_2} C_K$
$AB + K \overset{k_1}{\longrightarrow} AK^* + B$ $AK^* \overset{k_2}{\longrightarrow} K + A$	$r = \dfrac{k_1 k_2 C_{AB}}{k_1 C_{AB} + k_2} C_K$	K ⇄ AK* (ω_1, ω_2)	$D_K = \omega_2$ $D_{AK^*} = \omega_1$	$r = \dfrac{k_1 k_2 C_{AB}}{k_1 C_{AB} + k_2} C_K$
$AB + K \overset{k_1}{\longrightarrow} ABK^*$ $ABK^* \overset{k_2}{\longrightarrow} A + B + K$		K ⇄ ABK* (ω_1, ω_2)	$D_K = \omega_2$ $D_{ABK^*} = \omega_1$	

Some catalytic redox reactions used frequently in the kinetic methods of analysis are actually two step reactions. Considering for example the catalytic oxidation of iodide by halates [10] using vanadium compounds as catalysts, an oxidation of vanadium (IV) to vanadium (V) by halate and a reduction of vanadium (V) to vanadium (IV) by iodide occurs alternatively. It can be easily shown that such a reaction can be represented by a two step mechanism and by the corresponding graph [10] which can be treated from the kinetic standpoint similarly to those previously shown.

Another reaction which is worth mentioning is the catalytic decomposition of hydrogen peroxide by the coordination compounds of nickel with monoethanolamine [30] which occurs according to the two step mechanism:

$$Ni(MEA)_n^{2+} + H_2O_2 \rightleftarrows Ni(MEA)_n^{2+} \cdot H_2O_2$$

$$Ni(MEA)_n^{2+} \cdot H_2O_2 + H_2O_2 \rightarrow Ni(MEA)_n^{2+} + 2H_2O + O_2$$

and which is described by a sheme which is relatively similar to that given in the second row of table 1.Under such conditions one can directly write the rate equation:

$$r = \frac{k_1 k_2 C^2_{H_2O_2}}{k_1 c_{H_2O_2} + k_{-1} + k_2 c_{H_2O_2}} C_{Ni(MEA)_n^{2+}} \tag{8}$$

Which is quite similar to that obtained by means of QSSA.

Conclusions

The use of graph in kinetic analysis offers simple rigorous and efficient procedures to write kinetic equations. In many cases such procedures allow to bypass the cumbersome calculations required by QSSA.

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