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FLOW GRAPHS IN CHEMICAL KINETICS (I)

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ABSTRACT. Flow graphs used in physics and electronics have been applied to chemical kinetics. Rate laws and expressions of various concentrations of species involved in the mechanisms have been described for several simple systems. Flow graphs were constructed in agreement with the mechanism and differential equations that characterize the time evolution of molecules or radicals involved, and the characteristic determinants for the system. A short introduction of basic principles of flow graphs, their properties and algebra are also presented. The same results were straightly obtained as those resulted from classical integration or by applying quasi-steady-state approximation.

Introduction

Graphs and diagrams of various types have been used to depict reaction mechanisms in chemistry as chain processes, catalyzed processes, and enzyme-catalyzed processes[1-2]. Temkin[3-5] has proposed a convenient version of cyclic graphs. These graphs incorporate only intermediate species as vertices. They were used to deduce - in a quite simple way - the concentration of reactive intermediates and the overall reaction rate[6-8]. Numerous chemical chain reactions, photochemical reactions involving propagation of chain as elementary steps, enzyme-catalyzed reactions or even heterogeneous reactions were approached this way. Temkin and Bonchev and their co-workers[9-12] have classified various types of complex mechanisms on the ground of graphs associated with these mechanisms.

Inspired by the flow graphs used in electronics, physics and engineering[13-15], we show in this work haw to use flow graphs to associate them with reaction mechanisms in order to obtain some kinetic characteristics of any reaction scheme. Besides the intermediates, these graphs incorporate also the starting chemical species, the main and secondary products. At the same time, we associated determinants to chemical change and construct graphs on this base. Our approach has the advantage of offering the opportunity to calculate the concentration of any species involved either being in a quasi-steady-state or a transient concentration. These flow graphs can be used for various types of mechanisms with linear sequence, opposing processes, single route chain reactions, homogeneous and heterogeneous catalyzed reactions.

Some basic principles of flow graphs

A flow graph is a diagram that represents a set of simultaneous linear algebraic situations (linear differential equations)[13]. It is used to represent a system and to obtain the relationships among the system variables. By using the Cramer method[16] with determinants one could solve the system.

A flow graph consists of a network in which nodes (or vertices) are connected by directed edges (or branches). Each node (vertex) represents a system variable, and each edge connected between two vertices acts as a signal multiplier. An arrow placed on the edge indicates the direction of a signal flow and the multiplication factor is indicated along the edge. This multiplication factor is named transmittance and it can be obtained from the coefficients of the equations. The signal flow graph depicts the flow of signals from one point of the system to another and gives the relationships among the signals and it describes the determinant of the system[13].

Definitions related to flow graphs. Before discussing flow graphs certain terms should be defined:

Node (Vertex) is a point representing a variable or a signal. In chemistry it represents a chemical species undergoing some transformation.

Edge (branch) is a directed line segment joining two nodes. The gain of a branch is the transmittance.

Weighting of an edge (transmittance) is a real or complex gain between nodes. Such gains can be expressed in terms of transfer function between two nodes. In chemical kinetics it represents a pseudo-first- or a true first-order rate constant measuring the frequency with which chemical event takes place. By multiplying it with the actual concentration of the species in the vertex of outgoing branch and the volume of the system, the chemical flux, in the indicated direction, is obtained.

Input node or source is a node that has only outgoing edges. This corresponds to an independent variable. In chemical kinetics it represent the reactant species.

Output node or sink is a node that has only incoming edges. This corresponds to a dependent variable. In chemical kinetics, it corresponds to a reaction product.

Mixed (internal) node is one that has both outgoing and incoming edges.

Path or way is a traversal of connected branches in the direction of the branch arrows.

Forward path (way) is a path from an input node (source) or from a mixed node, if the source is missing, to an output node (sink). The way should not visit any node more than once.

Forward path gain is the product of the branch transmittances of a forward path. A flow graph example is presented in figure 1.

*Properties of flow graphs***.** A few important proprieties of flow graphs are as follows:

A branch indicates the functional dependence of one signal on another.

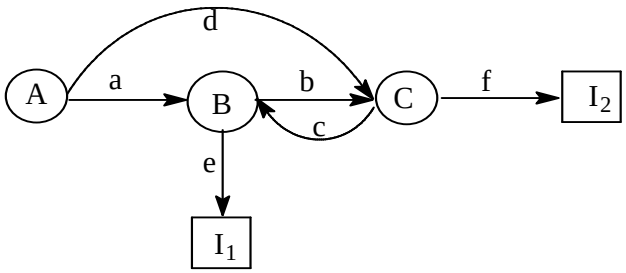


Fig.1. An example of a flow graph. A is an input node (source); I_1 I_2 are output nodes (sinks); a, b, c, d, e, and f are weighting of the edges; B, C are the internal nodes.

A signal passes trough only in the direction specified by the arrow of the branch.

A node adds the signals of all incoming branches and transmits their sum to all outgoing branches.

An interval node, which has both incoming and outgoing branches, may be viewed as an output node by ignoring its outgoing branches. Note, however, that a mixed node never can be a source (input node) in this approach.

For a given system a flow graph is not unique. More than one flow graphs can be drawn for a given system by writing the system equations or the corresponding determinants in a different way[13-15].

Flow graphs algebra. A flow graph of a linear system can be drawn using the above definitions. The independent and dependent variables of the equations become the input nodes and the other nodes respectively. To determine these variables, the system is solved by using the Cramer method. Each value is a ratio of two determinants. From the reaction mechanism, the system of equations and corresponding determinants can be written. On the determinants base the flow graph can be constructed by following some rules. A simple example related to figure 1 is given bellow:

$$\begin{cases} (b+e)[B] - c[C] = a \\ -b[B] + (c+f)[C] = d \end{cases} \qquad (1)$$

and $[I_1]=e[B]$, $[I_2]=f[C]$

Laplacian matrix of the system is defined by the formula (2)[17]:

$$La(G) = Deg(G) - A(G) \qquad (2)$$

To form the flow graph for this determinant, which characterizes the system, the rules are[18]:

1. The above determinant can be written as:

$$\Delta = \begin{vmatrix} b + e & -c \\ -b & c + f \end{vmatrix} \tag{3}$$

2. The variables become nodes in the graph: the variables from the system (B and C) become the mixed nodes and I_1 and I_2 turn into output nodes.

3. The branch transmittance can be obtained from the coefficients of the system as follows:

-The element of line 1, column 1 represents all the transmittances of the edges, which are outgoing from the node B with the sign plus.

-The element of line 1, column 2 represents transmittance of edge outgoing from C and incoming to B with the sign minus in front of it, because it means a decrease of C variable.

The line 2 is obtained in the same way. The flow graph is presented in figure 2:

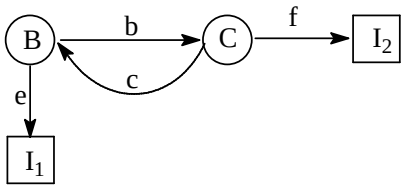


Fig. 2. The flow graph of the main determinant

The reciprocal of the above discussion is also valid. The main determinant of the system can be derived from this flow graph.

By tacking into account this flow graph and by using its properties given above, the global gain of the flow graph, which is the value of the main determinant, can be computed[18]. The global gain of the flow graph is the sum of the forward path gain, considering every possible way, and is represented in figure 3:

The global gain of the flow graph, which is the value of the determinant, is the sum of the all-possible forward path gain:

$$\Delta = \Delta_1 + \Delta_2 + \Delta_3 \tag{4}$$

In accordance with the definition concerning the visit of a node, the paths presented in the figure 4 cannot be considered because, in these cases, the nodes B and C have two output branches respectively. They were already considered as separate ways in figure 3. Also, the cyclic form (figure 5) cannot be considered because it disagrees with the mass conservation and has not any flux to an output node.

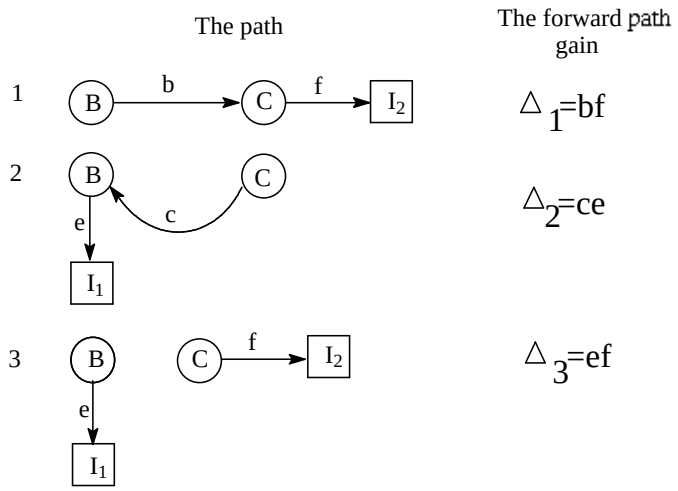


Fig. 3. The global gain of the flow graph.

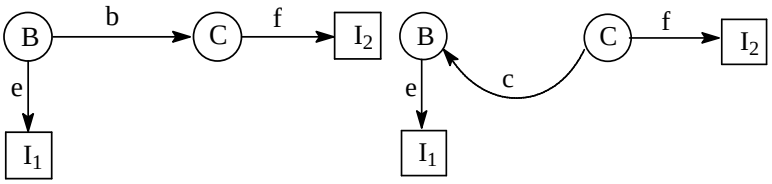


Fig. 4. Nodes with two output branches

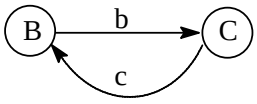


Fig. 5. Cyclic branches

As stated above, in order to calculate the dependent variables of the system, the species are considered target species or output nods. The corresponding determinant for their formation are:

$$\Delta_B = \begin{array}{c} \\ B \\ C \end{array}\begin{array}{c} \begin{array}{cc} A & C \end{array} \\ \begin{vmatrix} a & -c \\ d & c+f \end{vmatrix} \end{array} \quad \text{and} \quad \Delta_C = \begin{array}{c} \\ B \\ C \end{array}\begin{array}{c} \begin{array}{cc} B & A \end{array} \\ \begin{vmatrix} b+e & a \\ -b & d \end{vmatrix} \end{array} \quad \text{where} \begin{array}{c} A \\ \begin{pmatrix} a \\ d \end{pmatrix} \end{array} \qquad (5)$$

is the matrix of the free coefficients. They are the transmittances of the independent variable (the input node A). The sign plus is attributed to *a* and *d* in the determinant because positive gains of B and C occur from the input node A.

The flow graph for the determinant Δ_B, where B becomes an output node (figure 6):

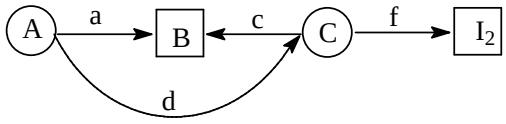


Fig. 6. The flow graph for Δ_B

and his value calculated from the above rules is :

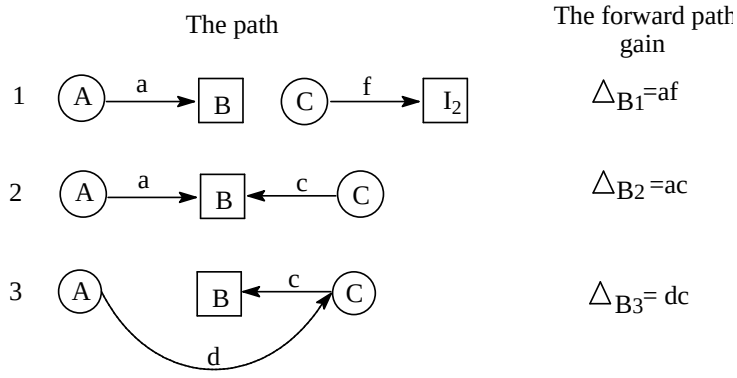


Fig. 7. Schematic ways to compute Δ_B.

The way through *d* and *f*, Δ_{B4}= df, is not considered because the target species B is not visited. The value of the determinant corresponding to B species is:

$$\Delta_B = \Delta_{B1} + \Delta_{B2} + \Delta_{B3} = af + ac + dc \quad (6)$$

In the same way, when C is the output node Δ_C is obtained as Δ_C = ab+bd+ed following the same rules as shown in figure 8.

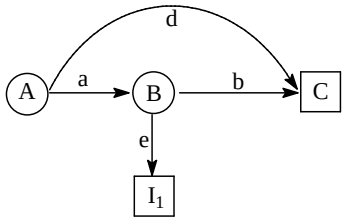


Fig. 8. The flow graph for Δ_C

If all three graphs are combined, the global graph can be constructed. It represents the flow graph for the system (eq. 7) as a whole[14,15,18], as presented in figure 1.

$$\begin{array}{c} \\ B \\ C \end{array}\left\{\begin{array}{ccc} B & C & A \\ (b+e)[B] & -c[C] & = a \\ -b[B] & +(c+f)[C] & = d \end{array}\right. \qquad \begin{array}{c} \\ B \\ C \end{array}\left(\begin{array}{ccc} B & C & A \\ b+e & -c & -a \\ -b & c+f & -d \end{array}\right) \tag{7}$$

Application to methane pyrolysis.

The first example to be discussed is the methane pyrolysis. The following elementary processes represent the simple mechanism[19], when the reverse reactions are not considered:

$$\begin{aligned} &CH_4 \xrightarrow{k_1} CH_3^{\cdot} + H^{\cdot} && k_1 = 4.3*10^{-6}\ s^{-1} \\ &CH_3^{\cdot} + CH_4 \xrightarrow{k_2} C_2H_6 + H^{\cdot} && k_2 = 6.57*10^{5}\ L/mol\ s \\ &H^{\cdot} + CH_4 \xrightarrow{k_3} CH_3^{\cdot} + H_2 && k_3 = 4*10^{8}\ L/mol\ s \\ &2CH_3^{\cdot} \xrightarrow{k_4} C_2H_6 && k_4 = 9.0125*10^{9}\ L/mol\ s \end{aligned} \tag{8}$$

The accepted values of the rate constants are also given. The stoichiometry is represented by the equation:

$$2CH_4 \rightarrow C_2H_6 + H_2 \tag{9}$$

In this case, the quasi steady state approximation (QSSA) can be applied for the active radicals. Their steady state concentrations are:

$$[CH_3\cdot] = \sqrt{\frac{k_1}{k_4}[CH_4]} \qquad [H\cdot] = \frac{k_2}{k_3}\sqrt{\frac{k_1}{k_4}}[CH_4]^{\frac{1}{2}} \tag{10}$$

According to the mechanism (8), the rate law is obtained as the summation of the two steps yielding ethane:

$$r = \frac{d[C_2H_6]}{dt} = k_2[CH_3\cdot][CH_4] + k_4[CH_3\cdot]^2 \tag{11}$$

and therefore

$$r = k_2\sqrt{\frac{k_1}{k_4}}[CH_4]^{3/2} + k_1[CH_4] \tag{12}$$

By taking into account the values of the rate coefficients it simplifies to the form:

$$r = k_2\sqrt{\frac{k_1}{k_4}}[CH_4]^{3/2} \tag{13}$$

An alternative way of dealing with the system is to use the flow graph method. The differential equations for the reaction system are:

$$\begin{cases} \dfrac{d[CH_3^{\cdot}]}{dt} = 0 = (k_2 a + 2k_4 x)[CH_3^{\cdot}] - k_3 a[H^{\cdot}] - k_1[CH_4] \\ \dfrac{d[H^{\cdot}]}{dt} = 0 = -k_2 a[CH_3^{\cdot}] + k_3 a[H^{\cdot}] - k_1[CH_4] \end{cases} \tag{14}$$

The following notations are used further on: $[CH_4] = a$ and $[CH_3^{\cdot}] = x$. With these the following equations ca be written:

$$\begin{cases} k_1 a = (k_2 a + 2k_4 x)[CH_3^{\cdot}] - k_3 a[H^{\cdot}] \\ k_1 a = -k_2 a[CH_3^{\cdot}] + k_3 a[H^{\cdot}] \end{cases} \tag{15}$$

Here the matrix of the free coefficients represents the matrix of the transmittances of branches outgoing from the input node

$$\begin{array}{c} \\ CH_3^{\bullet} \\ H^{\bullet} \end{array} \begin{array}{c} \begin{array}{cc} CH_3^{\bullet} & H^{\bullet} \end{array} \\ \begin{pmatrix} k_2 a + 2k_4 x & -k_3 a \\ -k_2 a & k_3 a \end{pmatrix} \end{array} \begin{pmatrix} CH_3^{\bullet} \\ H^{\bullet} \end{pmatrix} = \begin{array}{c} CH_4 \\ \begin{pmatrix} k_1 a \\ k_1 a \end{pmatrix} \end{array} \tag{16}$$

$$A \quad \cdot \quad B \quad C$$

The flow graph is the one in which we can transpose the extended determinant (16), as has been shown above, *obtaining a perfect image of the mechanism* (figure 9)

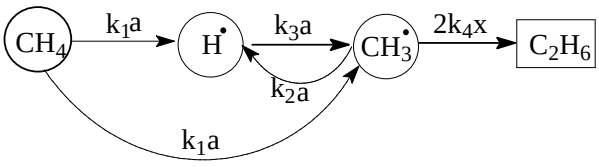


Fig. 9. Flow graph for methane pyrolysis

where C_2H_6 is the final product of termination step (the output node) and CH_4 is the main reactant (the input node). The starting species CH_4, the radical species $CH_3\cdot$ and $H\cdot$ and the final product C_2H_6 represent the nodes and the pseudo-first order rate constants k_1, k_2a, k_3a, and $2k_4[CH_3\cdot]$ represent the branch transmittance, obtained from the coefficients of the system.

The main determinant, or *the global consumption of the radicals' determinant*, is that one of matrix A denoted here by Δ:

$$\text{det. A} = \Delta = \begin{vmatrix} k_2 a + 2k_4 x & -k_3 a \\ -k_2 a & k_3 a \end{vmatrix} = 2k_4 x\, k_3 a \tag{17}$$

The value of *main determinant is also equal with the global gain of the flow graph, without considering the reactant (the input node).* Therefore it can be obtained straight from the graph by multiplying the branch transmittances which are outgoing from radicals to the final product, taking into account every possible ways and every radical involved in the mechanism.

The determinant for $CH_3\cdot$, *the formation determinant* is:

$$\Delta_x = \begin{vmatrix} k_1 a & -k_3 a \\ k_1 a & k_3 a \end{vmatrix} = 2k_1 a k_3 a \tag{18}$$

The value of the formation determinant *is also equal with the gain of flow graph considering the radical species an output node*. It is obtained by adding the product of transmittance of the branches, which are outgoing from the reactant CH_4 to the target radical on every possible ways, using the rules of the flow graphs.

The radical concentration CH_3, can be obtained by applying the Cramer rules in the same way as King and Altman did for enzyme catalyzed reactions[2]:

$$x = [CH_3\cdot] = \frac{\Delta_x}{\Delta} = \frac{2ak_1k_3a}{2k_4xk_3a} \quad ; \quad x = \sqrt{\frac{k_1}{k_4}a} \tag{19}$$

Thus, the determinant for H·(the formation determinant for H· species) is:

$$\Delta_{H\cdot} = \begin{vmatrix} k_2 a + 2k_4 x & k_1 a \\ -k_2 a & k_1 a \end{vmatrix} = 2k_1 a k_2 a + 2k_4 x k_1 a \tag{20}$$

$$[H\cdot] = \frac{2ak_1k_2a + 2ak_4xk_1}{2k_4k_3a\sqrt{\frac{k_1}{k_4}a}} \cong \frac{2ak_1k_2a}{2k_4k_3a\sqrt{\frac{k_1}{k_4}a}} = \sqrt{\frac{k_1}{k_4}} \cdot \frac{k_2}{k_3} a^{1/2} \tag{21}$$

Finally, the rate law,

$$r = k_2 \sqrt{\frac{k_1}{k_4}} [CH_4]^{3/2} \tag{22}$$

is identical with the one obtained by the quasi-steady-state approximation.

Application to a series of first-order reactions

The next goal of the present work is to analyze an infinite series of consecutive first-order reactions:

$$A_1 \xrightarrow{k_1} A_2 \xrightarrow{k_2} A_3 \xrightarrow{k_3} \ldots \xrightarrow{k_{i-1}} A_i \xrightarrow{k_i} \ldots \tag{23}$$

The concentration of the first term in the series is calculated by solving the simple differential equation: $-d[A]/dt = k_1[A]$ yielding the solution $[A]=[A]_0 e^{-k_1 t}$. The last term concentration in the series, which is the final product, can be calculated from the mass balance. It is obvious that the concentration of any species depends on the concentrations of all previous species, starting from the reactant A_1. By using the Cramer method, the linear system of the differential equations can be solved. It follows that:

$$[A_i]=f([A_j])_{\overline{j=1,i}};\quad [A_i]=\sum_{j=1}^{i} B_j e^{-\gamma_j t}=\sum_{j=1}^{i} B_j e^{-k_j t} \text{ for i = 2,n-1; } B_j=\frac{\Delta_i}{\Delta_{B_j}} \quad (24)$$

where γ_j is the exponential factor and, in this case, the factors are equal with the rate constants [20] and B_j is an irreducible ratio found after simplifications of common terms. For the determination of $[A_i]$ one has to calculate "i" coefficients: B_1, B_2, B_3,… B_i; therefore there is a number of *i* determinants Δ_{Bj}. The term $B_j e^{-k_j t}$ represents the contribution of species *j* at the formation of species *i* as part of the ensemble formed by all the species: *i* and the precursors.

Δ_i is the determinant which indicate *the formation of species* A_i and it is calculated directly from the principal flow graph, representing the mechanism, following the rules already given. The value of the determinant is equal to the flow graph gain: product of the branch transmittance of a forward path that goes to the formation of species *i* from the reactant A_1 as indicated in figure 10.

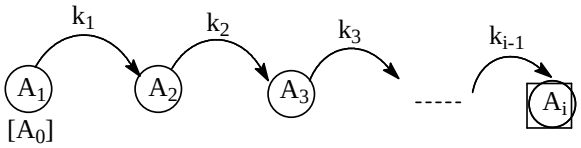


Fig. 10. The formation flow graph of A_i species.

Therefore

$$\Delta_i=[A_0]k_1k_2...k_{i-1}=[A]_0\prod_{j=1}^{i-1}k_j \quad (25)$$

We have shown, in the case of chain reaction, that the main determinant (in the denominator) suggests a flow graph without the input node, the reactant that provides the formation of the specie involved. It is named *the global consumption determinant* because it indicates the consumption of all species in the favor of products.

Δ_{B_j} - *the global consumption determinant -,* being part of the term ($B_j e^{-k_j t}$), which refers to the contribution of "j" species to the formation of "i" species, it is obtained as a sub-graph that result from the principal flow graph, representing the mechanism, by eliminating the species "j", with his corresponding rate constant. Then one has to subtract k_j from every rate constant on the branches and eliminate A_j: It is shown in the figure 11.

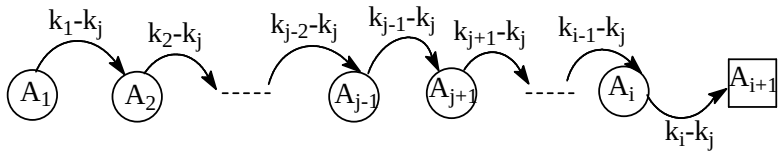


Fig. 11. The consumption flow graph of the term $B_j e^{-k_j t}$

The phenomenological explanation consists in the fact that *consumption of any intermediate species concentration involved could not occur before this species is formed. (the rate of consumption cannot exceed the rate of its formation).*

$$\Delta_{B_j} = (k_1 - k_j)(k_2 - k_j)...(k_{j-2} - k_j)(k_{j-1} - k_j)(k_{j+1} - k_j)...(k_{i-1} - k_j)(k_i - k_j)$$
$$= \prod_{l=1;l\neq j}^{i}(k_l - k_j) = \prod_{l=1;l\neq j}^{i}(\gamma_l - \gamma_j) \quad (26)$$

By tacking into account the graph in figure 10, the formation determinant for the *i* species is:

$$\Delta_i = \begin{vmatrix} k_1 & 0 & 0 & 0 & 0 & 0 \\ -k_1 & k_2 & 0 & ..... & & \\ ..... & ..... & ..... & ..... & & \\ 0 & .....k_{j-1} & k_j & .....0 & & \\ ..... & ..... & ..... & ..... & & \\ 0 & ..... & ..... & .....0 & k_{i-1} & \end{vmatrix} = \prod_{j=1}^{i-1} k_j \quad (27)$$

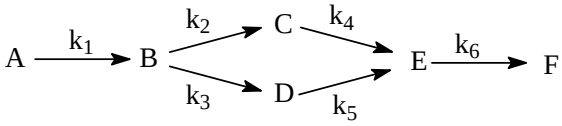
and the consumption determinant, in accordance with figure 11 is[20]:

$$\Delta_{B_1} = \begin{vmatrix} (k_2 - k_1) & 0 & 0 & 0 & 0 & 0 \\ -(k_2 - k_1) & (k_3 - k_1) & ..... & & & \\ 0 & ..... & ..... & ..... & ..... & 0 \\ ..... & ..... & (k_{j-1} - k_1) & (k_j - k_1) & ..... & 0 \\ ..... & ..... & ..... & ..... & ..... & \\ 0 & ..... & ..... & ..... & ..... & k_{i-1} \end{vmatrix} = \prod_{j=2}^{i}(k_j - k_1) = \prod_{j=2}^{i}(\gamma_j - \gamma_1) \quad (28)$$

By using these determinants the concentration of each species in the mechanism is obtained and it is the same as obtained by classical integration of the system[21].

Application to a mixed series and parallel reactions.

Another relevant example, encountered in the case or radioactive series, more complex in the sense it contains parallel processes, is:



(29)

It starts from $[A]_0$ in the absence of any intermediate or final product. The starting species concentration decays exponentially. To calculate [B] a new flow graph should be constructed. It is a basic flow graph, for global consumption of B species, as presented in figure 12:

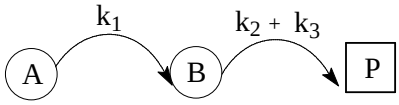


Fig. 12. For the consumption of B scheme

P stands for the products coming from B species when it reacts.

$$[B]=\sum_{j=1}^{2} B_j e^{-\gamma_j t} \text{ with the coefficients } {}^{20}$$
$$B_j=\frac{\Delta_i}{\Delta_{B_j}};\quad \gamma_{j=1}=k_1;\quad \gamma_{j=2}=k_2+k_3=k_2^{'} \tag{30}$$

Δ_i is the formation determinant and it can be calculated directly from mechanism (29) starting from A to the specie (B); Δ_{Bj} is the consumption determinant and it is obtaining eliminating the species one after another from the basic flow graph for the consumption(fig.12):

$$\Delta_i=[A]_0 k_1;\quad \Delta_{B_1}=k_2^{'}-k_1\ ;\Delta_{B_2}=k_1-k_2^{'};\quad [B]=\frac{k_1[A]_0}{k_2^{'}-k_1}(e^{-k_1 t}-e^{-k_2^{'}}) \tag{31}$$

In order to calculate [C] one has to construct a new basic flow graph, the one for global consumption:

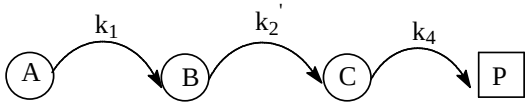


Fig. 13. The consumption flow graph for determining [C].

$$\Delta_i = [A]_0 k_1 k_2; \qquad \Delta_{B_1} = (k_2^{'} - k_1)(k_4 - k_1) \tag{32}$$

$$\Delta_{B_2} = (k_1 - k_2^{'})(k_4 - k_2^{'}); \quad \Delta_{B_3} = (k_1 - k_4)(k_2^{'} - k_4) \tag{33}$$

$$[C] = \frac{[A]_0 k_1 k_2 e^{-k_1 t}}{(k_2^{'} - k_1)(k_4 - k_1)} + \frac{[A]_0 k_1 k_2 e^{-k_2^{'} t}}{(k_1 - k_2^{'})(k_4 - k_2^{'})} + \frac{[A]_0 k_1 k_2 e^{-k_4 t}}{(k_1 - k_4)(k_2^{'} - k_4)} \tag{34}$$

Similar for determination [D]:

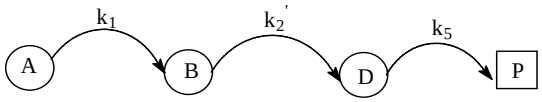


Fig. 14. The consumption flow graph for determining [D].

$$[D] = \frac{[A]_0 k_1 k_3 e^{-k_1 t}}{(k_2^{'} - k_1)(k_5 - k_1)} + \frac{[A]_0 k_1 k_3 e^{-k_2^{'} t}}{(k_1 - k_2^{'})(k_5 - k_2^{'})} + \frac{[A]_0 k_1 k_3 e^{-k_5 t}}{(k_1 - k_5)(k_2^{'} - k_5)} \tag{35}$$

The global consumption determinants for [E] results from the two basic flows graph (figure 15) because there are two different ways to obtain it.

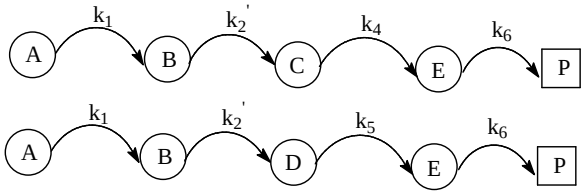


Fig. 15. The two ways of consumption of E species

$$\frac{[E]}{[A]_0} = \frac{k_1 k_2 k_4 e^{-k_1 t}}{(k_2^{'} - k_1)(k_4 - k_1)(k_6 - k_1)} + \frac{k_1 k_2 k_4 e^{-k_2^{'} t}}{(k_1 - k_2^{'})(k_4 - k_2^{'})(k_6 - k_2^{'})} + \\ + \frac{k_1 k_2 k_4 e^{-k_4 t}}{(k_1 - k_4)(k_2^{'} - k_4)(k_6 - k_4)} + \frac{k_1 k_2 k_4 e^{-k_6 t}}{(k_1 - k_6)(k_2^{'} - k_6)(k_4 - k_6)} + \\ + \frac{k_1 k_3 k_5 e^{-k_1 t}}{(k_2^{'} - k_1)(k_5 - k_1)(k_6 - k_1)} + \frac{k_1 k_3 k_5 e^{-k_2^{'} t}}{(k_1 - k_2^{'})(k_5 - k_2^{'})(k_6 - k_2^{'})} + \\ + \frac{k_1 k_3 k_5 e^{-k_5 t}}{(k_1 - k_5)(k_2^{'} - k_5)(k_6 - k_5)} + \frac{k_1 k_3 k_5 e^{-k_6 t}}{(k_1 - k_6)(k_2^{'} - k_6)(k_5 - k_6)} \tag{36}$$

The final species concentration is obtained from the mass balance:

$$[A]_0\text{-}[A]\text{-}[B]\text{-}[C]\text{-}[D]\text{-}[E] = [F] \tag{37}$$

A new approach of methane pyrolysis

The same way of treatment can be applied to the methane pyrolysis in its simple mechanism presented above, considered as an open sequence. If QSSA is not taken into consideration, from the flow graph depicted in figure 9, the global determinant, which provides the exponential factor, is[20,22]:

$$\Delta_\gamma = \begin{vmatrix} k_2 a + 2k_4 x - \gamma & -k_3 a & -k_1 \\ -k_2 a & k_3 a - \gamma & -k_1 \\ 0 & 0 & 2k_1 - \gamma \end{vmatrix} = 0 \quad (38)$$

$$\Delta_\gamma = (2k_1-\gamma)[\gamma^2-\gamma(k_2 a + k_3 a + 2k_4 x)+ 2k_4 x\, k_3 a = 0 \quad (39)$$

where $[CH_3^{\cdot}] = x$, $\gamma_1 = 2k_1$, $\gamma_2 \approx k_3 a$ and $\gamma_3 \approx 2k_4 x$. Because the transformation of the intermediate species is considered now as consecutive steps, the methyl radical concentration is:

$$x = \frac{2ak_1k_3a}{(\gamma_2-\gamma_1)(\gamma_3-\gamma_1)}e^{-\gamma_1 t} + \frac{2ak_1k_3a}{(\gamma_1-\gamma_2)(\gamma_3-\gamma_2)}e^{-\gamma_2 t} + \frac{2ak_1k_3a}{(\gamma_1-\gamma_3)(\gamma_2-\gamma_3)}e^{-\gamma_3 t} \quad (40)$$

$$x = \frac{2ak_1k_3a}{(k_3a-2k_1)(2k_4x-2k_1)}e^{-2k_1 t} + \frac{2ak_1k_3a}{(2k_1-k_3a)(2k_4x-k_3a)}e^{-k_3 a\, t} + \frac{2ak_1k_3a}{(2k_1-2k_4x)(k_3a-2k_4x)}e^{-2k_4 x\, t} \quad (41)$$

Now, considering that the terms two and three in the summation are much smaller than the first, a simpler expression is obtained:

$$x \approx \frac{2ak_1k_3a}{(k_3a-2k_1)(2k_4x-2k_1)}e^{-2k_1 t} \quad (42)$$

Because the first step rate coefficient is very small as compared to the others, the exponential is close to unity at least at the short reaction period $e^{-2k_1 t} \approx 1$, Consequently 2k1 << $2k_4x$ and $2k_1$ << k_3a. It results that:

$$x \approx \frac{2ak_1k_3a}{k_3a\,2k_4x} = \frac{ak_1}{k_4x} \qquad \text{or} \qquad x = \sqrt{\frac{ak_1}{k_4}} \quad (43)$$

which is the same result as the one obtained by applying QSSA method (see eq.10). The rate of the final product formation is $k_2ax + k_4x^2 \approx k_2ax$, the same as obtained by QSSA.

Various other complex mechanisms as the homogeneous catalyzed reactions, enzyme catalyzed reactions, single route chain reactions and multiple route chain reactions in the classification of Zeigarnik and Tenkin[11], will be

treated by using flow graph in the future papers of the series. They will involve situations where QSSA is used as well as opposing reactions, mixed series with opposing reactions, where QSSA is not appropriate.

Conclusions

The main conclusion concerning the flow graph employment in chemical kinetics is that a straight way to calculate the concentration of any species either for reactive intermediates or for transient intermediate, accumulating and decaying during the reaction.

In the case of the systems where QSSA is applicable, the flow graph is unique and the image of the reaction mechanism. In the case of open sequences, when the concentration of the intermediate species is not in a steady state, more than one graph should be considered. They can be constructed from the mechanism by taking into consideration several simple rules to form the formation and consumption determinants.

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