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FLOW GRAPH THEORY, AN ALTERNATIVE TO STEADY STATE APPROXIMATION

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ABSTRACT. Flow graphs used in physics and electronics have been applied to chemical kinetics. The expressions of various concentrations of species involved in various mechanisms have been described on the base of the signal flow graphs. 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. They were applied to substitution, enzyme catalyzed and chain reactions.

INTRODUCTION

Although the steady-state approximation has been used for almost a century[1] in describing complex mechanisms, the condition of constant concentration of the active intermediates is never fulfilled. *The method is said to entail setting to zero the first derivative of the concentration of each intermediates involved in the reaction mechanism.* Even in the well-known mechanism of HBr synthesis, the bromine atom concentration computed by steady-state approximation is in fact the one given by the dissociation of bromine molecule, that is an equilibrium concentration. The less severe condition of very small accumulation rate of intermediate as compared to the one of reactant consumption or product accumulation is in fact the quasi steady state approximation. It has been used for substitution reactions, non-equivalent redox reactions, chain reactions, acid-base catalytic reactions, enzyme catalyzed reactions, or heterogeneous catalyzed reactions. Several examples are discussed in this paper.

To show that, the consecutive reactions with reversible step is being chosen. The reaction sequence for the net transformation of A to C *via* reversible formation of intermediate B is:

$$\mathrm{A} \Leftarrow\Rightarrow \mathrm{B}, \quad \mathrm{k}_1, \mathrm{k}_{-1} \qquad \mathrm{B} \longrightarrow \mathrm{C} \quad \mathrm{k}_2 \tag{1}$$

The differential rate equations are:

$$\begin{aligned} \frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{dt}} &= \mathrm{k}_1[\mathrm{A}] - \mathrm{k}_{-1}[\mathrm{B}] \\ \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{dt}} &= \mathrm{k}_1[\mathrm{A}] - \mathrm{k}_{-1}[\mathrm{B}] - \mathrm{k}_2[\mathrm{B}] \\ \frac{\mathrm{d}[\mathrm{C}]}{\mathrm{dt}} &= \mathrm{k}_2[\mathrm{B}] \end{aligned} \tag{2}$$

In order to integrate them, the system can be simplified in certain circumstances to a far more tractable form. It consist on setting d[B]/dt= 0. A situation is a common one, and method finds wide application in many different chemical systems as enumerated above. As one can see, that is an unduly strict statement of the condition, which must be met to validate the method. Nonetheless, proceeding in this fashion for the moment and equating d[B]/dt to zero, the steady state concentration is:

$$[B]_{ss} = \frac{k_1[A]}{k_{-1} + k_2} \tag{3}$$

It reveals that the concentration of B is not constant but depends on the concentration of starting reactant A. As reaction proceeds, the starting material decays and the steady-state concentration of the intermediate declines. By substituting it to the rate expression of [A] consumption yields:

$$\frac{-d[A]}{dt} = k_1[A] - \frac{k_{-1}k_1[A]}{k_{-1} + k_2} = \frac{k_1 k_2 [A]}{k_{-1} + k_2} \tag{4}$$

and the accumulation of final product C is:

$$\frac{d[C]}{dt} = k_2[B] = \frac{k_1 k_2 [A]}{k_{-1} + k_2} \tag{5}$$

It results that the two rates -d[A]/dt and d[C]/dt are equal, as a consequence of setting d[B]/dt = 0. The conservation of mass requires

$$[A] + [B] + [C] = [A]_0$$

Actually, d[B]/dt is not zero. If it were, d[A]/dt would also be zero and no reaction would occur. Thus it seems worthwhile to examine more closely the nature of this approximation, so widely useful. It is necessary and sufficient condition for the validity of the above relations that

$$[B] \ll [A] + [C]$$

If it is so, from the material balance expressions

$$[A] = [A]_0 - [C] \qquad \text{or} \qquad [C] = [A]_0 - [A] - [C]$$

results the equality between the rate of consumption of A and accumulation of C. Another approach to exploring the nature of the steady-state approximation is based on the rearrangement of the rate expression of d[B]/dt to

$$[B] = \frac{k_1[A] - d[B]/dt}{k_{-1} + k_2} \tag{6}$$

By using this, the consumption of A is of the form

$$\frac{-d[A]}{dt} = \frac{k_1 k_2 [A]}{k_{-1} + k_2} + \frac{k_{-1} d[B]/dt}{k_{-1} + k_2} \tag{7}$$

This general equation contains a second term not found in steady-state solution. Another view of the condition needed to reduce this general solution to a simplified one resulting in steady-state approximation is:

$$\frac{d[B]}{dt} << \frac{k_1 k_2 [A]}{k_{-1}} \tag{8}$$

This is a condition[2] far less restrictive than the starting mathematical statement d[B]/dt = 0.

For the system with mixed consecutive and parallel processes

$A + B \Longleftrightarrow C$ $k_1, k_{-1};$ $C + D \rightarrow P$ $k_{2;}$

where C is an active intermediate, the condition of steady-state validity is:

$$\frac{d[C]}{dt} << \frac{k_1 k_2}{k_{-1}}[A][B][D] \tag{9}$$

These general rules were applied to various reaction systems as enumerated above. It is often important to compare the form of an experimental rate law with the one derived for the proposed mechanism. The rate law is expressed in terms of the concentrations of reactants, products, and catalysts in the reaction mixture, eliminating the concentrations of the reaction intermediates. The comparison is needed to learn whether each postulated mechanism is consistent with the data. For that reason one must develop some facility with the derivations.

Graphs and diagrams of various types have been used to depict reaction mechanisms in chemistry as chain processes, catalyzed processes, and enzyme-catalyzed processes[3,4]. Temkin[5-7] and Segal[8] have proposed a convenient version of cyclic graphs. These graphs incorporate only intermediate species as vertices and not starting materials and main or secondary products. They were used to deduce - in a quite simple way - the concentration of reactive intermediates and the overall reaction rate[9-14]. Inspired by the flow graphs used in electronics, physics and engineering[15-17], we show in this work how 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 constructed 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.

In dealing with complex reaction kinetics we have applied signal flow graph[18]. A flow graph is a diagram that represents a set of simultaneous differential equations connecting the system variables which could be solved by using Cramer method[15,19]. It consists of a network in which vertices or nodes, representing chemical species involved in the mechanism, are connected by edges acting as signal multipliers. These signal flow graphs (SFG) depict the flow of signals from one point of the system to another, give the relationships among signals and yield the determinants of the systems. We consider here the flow graphs for several examples where the steady state has been applied above in order to see how simple is this way to reach the steady-state concentration of intermediates or to find the rate law.

The basic principles of flow graphs, their properties, their algebra along with several applications have been presented previously[18].

APPLICATIONS

Monomolecular nucleophilic substitution. A classical example is the S_N1 mechanism for substitution in organic or inorganic chemistry. The replacement of H_2O from complexes $ML_6(H_2O)^{n+}$ by an anion Y^- has been found to be essentially first-order in both complex and substituting anion over a large range of conditions. Experiments of this kind are not entirely satisfactory with positively charged complexes because of complications brought about by ion-pair formation. To avoid this, anionic complexes were used. The concentration of $Co(CN)_5H_2O^{2-}$ has been found to conform to a S_N1 mechanism[20]:

$$\begin{aligned} &Co(CN)_5H_2O^{2-} \Longleftrightarrow Co(CN)_5^{2-} + H_2O \qquad k_1, k_2 \\ &Co(CN)_5^{2-} + Y^- \longrightarrow Co(CN)_5Y^{3-} \qquad k_3 \end{aligned} \tag{10}$$

with Y^- being Br^-, I^-, CN^-, CNO^-, OH^-. The steady-state concentration for pentacoordinate intermediate is:

$$[Co(CN)_5^{2-}]_{ss} = \frac{k_1[Co(CN)_5H_2O]}{k_2 + k_3[Y^-]} \tag{11}$$

and the rate law:

$$\frac{d[Co(CN)_5Y^{3-}]}{dt} = \frac{k_1k_3[Co(CN)_5H_2O][Y^-]}{k_2 + k_3[Y^-]} \tag{12}$$

The apparent first-order rate coefficient expression can be rearranged in a linear form. From various k_{obs} determined under various experimental conditions a various incoming ligands, a value of $k_1=1.6\text{x}10^{-3}\ s^{-1}$ has been found.

For this system the flow graph is depicted bellow[18]:

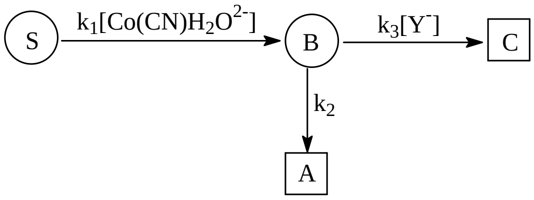

Fig.1. *The global flow graph*

where "S" represents the source of the interested species (B) or the input node, "B" is $Co(CN)_5^{2-}$, "C" is $Co(CN)_5Y^{3-}$ and "A" refers to $Co(CN)_5H_2O^{2-}$. It is observed that the reactant $Co(CN)_5H_2O^{2-}$ take place to the source and in the same time as an output node because it is formed in the first reversible reaction. The transmittances are the pseudo-first-order rate constants with respect to $Co(CN)_5^{2-}$ (B).

$$[Co(CN)_5^{2-}] = \frac{\text{The formation} \quad \text{determinant}}{\text{The consumption} \quad \text{determinant}} \tag{13}$$

The *formation flow graph* results from the main graph in which the interested species (B) becomes the target (the output node):

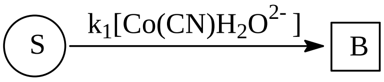

Fig. 2. *The formation flow graph of the species B*

$$\Delta_{formation} = k_1[Co(CN)H_2O^{2-}] \tag{14}$$

From the consumption determinant a graph (*the consumption flow graph*) is derived, which indicates the flowing from the transitional species to the output nodes and is obtained from the main flow graph eliminating the source:

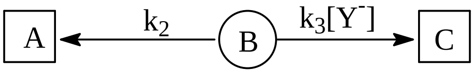

Fig. 3. *The consumption flow graph*

The value of the consumption determinant results from adding the transmittances of the independent ways to obtain a products[15-17]:

$$\Delta_{consumption} = k_2 + k_3[Y^-] \quad . \tag{15}$$

It results that

$$[Co(CN)_5^{-2}] = \frac{k_1[Co(CN)H_2O^{-2}]}{k_2 + k_3[Y^-]} \tag{16}$$

which is the same with that obtained above (11).

Enzymatic reactions. An representative example of enzymatic reaction is:

$$\begin{aligned} S + E &\Leftrightarrow X_1 && k_1,\ k_{-1} \\ X_1 + S &\rightarrow P + E && k_2 \\ X_1 &\Leftrightarrow X_2 && k_3,\ k_{-3} \\ X_2 &\rightarrow X_3 + E && k_4 \end{aligned} \tag{17}$$

with the rate law: $r = k_2[S][X_1]$.

By applying the QSSA, we obtain:

$$r = \frac{k_1k_2[S]^2[E]_0}{k_1[S] + k_2[S] + k_{-1} + \dfrac{k_1k_3[S]}{k_{-3}+k_4} + \dfrac{k_3k_4}{k_{-3}+k_4}} \tag{18}$$

The same results were obtained by King and Altman[4] using a schematic method of deriving the rate laws for enzyme catalyzed reactions, and also by Segal and co-workers[9,10] using the graph method. In the case of enzymatic reaction, the global signal flow graph is the perfect image of the mechanism:

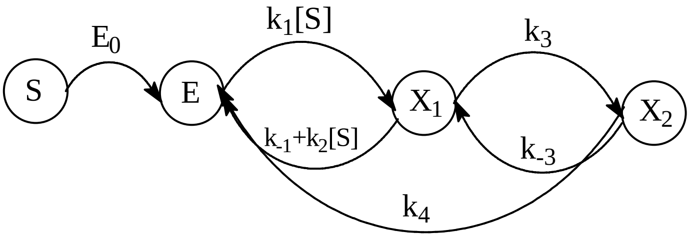

Fig. 4. *The global flow graph for enzymatic reaction*

The enzyme balance is $[E]+[X_1]+[X_2] = [E]_0$. The consumption of each species leads to the formation of the others species, so the consumption determinant could be written as a summation of three determinants[4] resulting from the flow graphs, characterized by the propriety that every species becomes the target species (the output node):

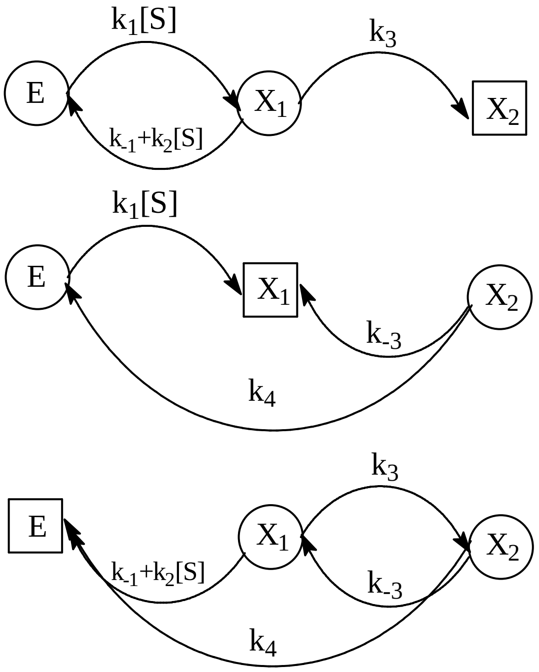

Fig. 5. *The consumption flow graphs of the implied specie*

Using the algebra properties of the flow graph[15-17,21] the consumption is:

$$\Delta_{consumption} = k_1[S]k_3 + (k_{-3} + k_4)k_1[S] + (k_{-3} + k_4)(k_{-1} + k_2[S]) + k_3k_4 \quad (19)$$

The formation flow graph for the intermediary "X_1" is:

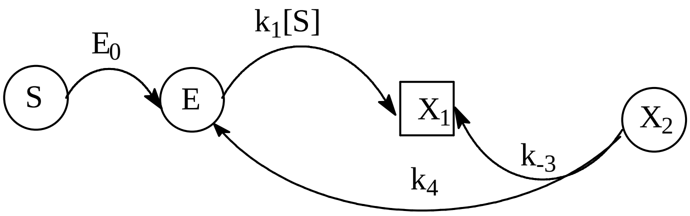

Fig. 6. *The formation flow graph for the species X_1*

"S" is the source or input node and represents, in this case, the initial concentrations of the involved species. The value of the formation determinant is:

$$\Delta_{X1} = E_0k_1[S]k_4 + E_0k_1[S]k_{-3} = E_0k_1[S](k_{-3} + k_4) \quad (20)$$

$$[X_1] = \frac{\Delta_{X1}}{\Delta_{consumption}} = \frac{E_0k_1[S](k_{-3} + k_4)}{k_1[S]k_3 + (k_{-3} + k_4)k_1[S] + (k_{-3} + k_4)(k_{-1} + k_2[S]) + k_3k_4} \quad (21)$$

Knowing that the rate law is $r = k_2[S][X_1]$ we obtain:

$$r = \frac{k_1k_2[S]^2[E]_0}{k_1[S] + k_2[S] + k_{-1} + \frac{k_1k_3[S]}{k_{-3} + k_4} + \frac{k_3k_4}{k_{-3} + k_4}} \quad (22)$$

which is the same result as that given by King and Altman[4] andE.Segal[9,10].

Chain Reactions. The application refers to gas decomposition of ethanal. The main reaction is:

$$CH_3CHO \rightarrow CH_4 + CO \quad (23)$$

and exhibits a fractional order 1.5 on ethanal. Trace quantities of C_2H_6 and H_2 were also detected in the products. Consider the following chain mechanism[22]:

Initiation	$CH_3CHO \rightarrow CH_3^{\cdot} + CHO^{\cdot}$	k_1	
	$CHO^{\cdot} \rightarrow CO + H^{\cdot}$	k_2	(24)
	$CH_3CHO + H^{\cdot} \rightarrow H_2 + CH_3CO^{\cdot}$	k_3	
Propagation	$CH_3^{\cdot} + CH_3CHO \rightarrow CH_4 + CH_3CO^{\cdot}$	k_4	
	$CH_3CO^{\cdot} \rightarrow CH_3^{\cdot} + CO$	k_5	
Termination	$2\,CH_3^{\cdot} \rightarrow C_2H_6$	k_6	

The formyl radical produced in the initiation reaction does not enter the chain reaction but gives the rise to secondary products. Making the steady state approximation, in order to eliminate the intermediate concentrations, one can derive the rate law:

$$\frac{d[CH_3]}{dt} = k_1[CH_3CHO] - k_4[CH_3CHO][CH_3] + k_5[CH_3CO] - 2k_6[CH_3]^2 = 0$$

$$\frac{d[CHO]}{dt} = k_1[CH_3CHO] - k_2[CHO] = 0$$

$$\frac{d[H]}{dt} = k_2[CHO] - k_3[H][CH_3CHO] = 0 \qquad (25)$$

$$\frac{d[CH_3CO]}{dt} = k_3[H][CH_3CHO] + k_4[CH_3][CH_3CHO] - k_5[CH_3CO] = 0$$

Addition of the steady-state conditions for the intermediates gives the result:

$$2k_1[CH_3CHO] = 2k_6[CH_3]^2 \quad ; \quad [CH_3]_{ss} = \sqrt{\frac{k_1[CH_3CHO]}{k_6}} \qquad (26)$$

and the rate is:

$$-\frac{d[CH_3CHO]}{dt} = 2k_1[CH_3CHO] + k_4\left(\frac{k_1}{k_6}\right)^{1/2}[CH_3CHO]^{3/2} \qquad (27)$$

This result is in agreement with the experimental rate law, provided the second term is much larger than the first. For long chain approximation, meaning that the substrate is consumed mainly in propagation step, this holds. Therefore, the experimental rate constant is:

$$k_{obsd} = k_4\left(\frac{k_1}{k_6}\right)^{1/2} \qquad (28)$$

The global flow graph of the equation system is a perfect image of the reaction mechanism[18]:

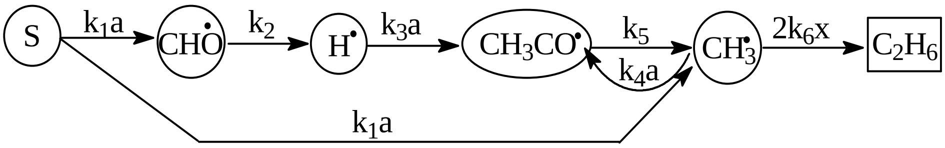

Fig. 7. *The global flow graph of system (24)*

where "S" represents the reactant CH_3CHO. The transmittances are the pseudo-first order rate constants with respect to the intermediate species; "a" means $[CH_3CHO]$ and "x" is $[CH_3]$.

The consumption flow graph is obtained from the system flow graph eliminating the source (input node):

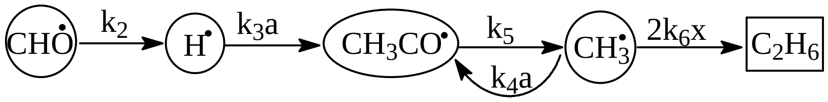

Fig. 8. *The consumption of the radical specie flow graph*

$$\Delta_{consumption} = k_2 \cdot k_3 a \cdot k_5 \cdot 2k_6 x \tag{29}$$

The formation flow graphs are drawn considering the species of interest as target nodes (output nodes). Their values are the product of the transmittances, starting from the source to the target species.

The formation flow graph for $CH_3^{\cdot}$ is:

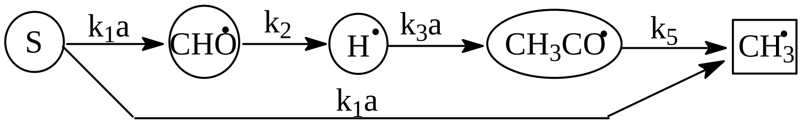

Fig. 9. *The formation of $CH_3^{\cdot}$ radical flow graph*

$$\Delta_{fCH3} = k_1 a \cdot k_2 \cdot k_3 a \cdot k_5 + k_1 a \cdot k_2 \cdot k_3 a \cdot k_5 = 2\, k_1 a \cdot k_2 \cdot k_3 a \cdot k_5 \tag{30}$$

$[CH_3] = x = \Delta_{fCH3} / \Delta_{consumption}$ and results:

$$k_1[CH_3CHO] = k_6[CH_3]^2 \quad ; \quad [CH_3] = \sqrt{\frac{k_1[CH_3CHO]}{k_6}} \tag{31}$$

which is the same result as discussed above.

The formation flow graph for $H^{\cdot}$ is:

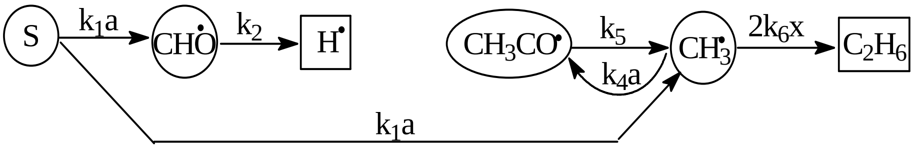

Fig. 10. *The formation of the $H^{\cdot}$ flow graph*

$$\Delta_{fH} = k_1 a \cdot k_2 \cdot k_5 \cdot 2k_6 x \tag{32}$$

Inserting the intermediate concentration obtained from the ratios of determinants into the rate law, gives:

$$-\frac{d[CH_3CHO]}{dt} = 2k_1[CH_3CHO] + k_4\left(\frac{k_1}{k_6}\right)^{1/2}[CH_3CHO]^{3/2} \tag{33}$$

which is identical to that obtained by applying the classical QSSA.

When one becomes accustomed to the flow graph all the formation or consumption determinants can be written directly from the global graph scheme and their concentrations calculated straightforward. The overall rate is immediately deduced. It avoids the need of detailed calculations with QSSA.

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