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***Dedicated to Professor Valer Fărcăşan***
***at his 85th anniversary***

# FLOW GRAPHS IN CHEMICAL KINETICS (II)

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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 radicals involved, and the characteristic determinants for the system. Short introduction 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.

**Keyword**: flow graph, differential equations, kinetics and mechanism

## 1. 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 [9-11] 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 [12-14], we tried 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 and the main or secondary products. At the same time, we associated determinants to chemical change and construct the graphs on this base. Such a way 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.

The purpose of this work is to introduce flow graphs and to show how to deal with them in solving some simple reaction mechanisms.

## 2. SOME BASIC PRINCIPLES OF FLOW GRAPHS

A flow graph is a diagram that represents a set of simultaneous linear algebraic situations (linear differential equations). It is used to represent a system and to obtain the relationships among the system variables. By using the Cramer's method[15] 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[16,17]. 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 represents the value of the determinant of the system[12].

### *Definitions related to flow graphs*

Before discussing flow graphs certain terms should be defined[18]:

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

*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.

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

*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 a node that has both outgoing and incoming branches.

*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.

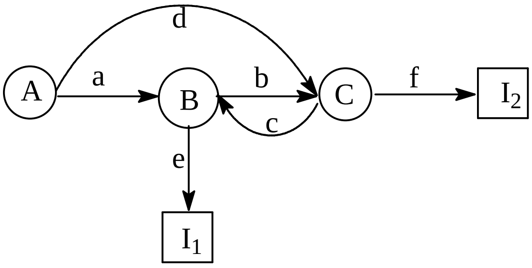

**Figure 1. An example of a flow graph. A is an input node (source); $I_1$ $I_2$ are output nodes (sinks); a, b, c, d, e, and f are weighting of the edges; B, C are the internal nodes.**

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[12-14].

### 3. APPLICATION TO METHANE PYROLYSIS

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

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

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

$$2CH_4 \rightarrow C_2H_6 + H_2 \qquad (2)$$

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

$$[CH_3\cdot] = \sqrt{\frac{k_1}{k_4}[CH_4]} \qquad [H\cdot] = \frac{k_2}{k_3}\sqrt{\frac{k_1}{k_4}}[CH_4]^{\frac{1}{2}} \qquad (3)$$

According to the mechanism (1), the rate law is obtained as the summation of the two steps yielding ethane:

$$r = \frac{d[C_2H_6]}{dt} = k_2[CH_3\cdot][CH_4] + k_4[CH_3\cdot]^2 \qquad (4)$$

and therefore

$$r = k_2\sqrt{\frac{k_1}{k_4}}[CH_4]^{3/2} + k_1[CH_4] \qquad (5)$$

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

$$r = k_2\sqrt{\frac{k_1}{k_4}}[CH_4]^{3/2} \qquad (6)$$

An alternative way of dealing with the system is to use the flow graph method.

The differential equations for the reaction system are:

$$\begin{cases} \dfrac{d[CH_3^{\cdot}]}{dt} = 0 = (k_2a + 2k_4x)[CH_3^{\cdot}] - k_3a[H^{\cdot}] - k_1[CH_4] \\ \dfrac{d[H^{\cdot}]}{dt} = 0 = -k_2a[CH_3^{\cdot}] + k_3a[H^{\cdot}] - k_1[CH_4] \end{cases} \qquad (7)$$

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

$$\begin{cases} k_1a = (k_2a + 2k_4x)[CH_3^{\cdot}] - k_3a[H^{\cdot}] \\ k_1a = -k_2a[CH_3^{\cdot}] + k_3a[H^{\cdot}] \end{cases} \qquad (8)$$

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

$$\begin{array}{cc} & \begin{array}{cc} CH_3^{\bullet} & H^{\bullet} \end{array} \\ \begin{array}{c} CH_3^{\bullet} \\ H^{\bullet} \end{array} & \begin{pmatrix} k_2a+2k_4x & -k_3a \\ -k_2a & k_3a \end{pmatrix} \end{array} \begin{pmatrix} CH_3^{\bullet} \\ H^{\bullet} \end{pmatrix} = \overset{CH_4}{\begin{pmatrix} k_1a \\ k_1a \end{pmatrix}} \qquad (9)$$

$$A \cdot B \quad C$$

The flow graph is the one in which we can transpose the extended determinant, as has been shown above, *obtaining a perfect image of the mechanism* (figure 2).

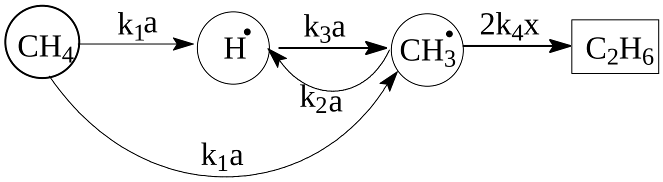

**Figure. 2. Flow graph for methane pyrolysis**

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:

$$\text{det. A } = \Delta = \begin{vmatrix} k_2a + 2k_4x & -k_3a \\ -k_2a & k_3a \end{vmatrix} = 2k_4x\,k_3a \tag{10}$$

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:

$$\Delta_x = \begin{vmatrix} k_1a & -k_3a \\ k_1a & k_3a \end{vmatrix} = 2k_1ak_3a \tag{11}$$

The value of the formation determinant *is also equal with the gain of flow graph considering the radical specie 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's rules in the same way as King and Altman did for enzyme catalyzed reactions[2]:

$$x = [CH_3\cdot] = \frac{\Delta_x}{\Delta} = \frac{2ak_1k_3a}{2k_4xk_3a} \quad ; \quad x = \sqrt{\frac{k_1}{k_4}a} \tag{12}$$

Thus, the determinant for $H\cdot$(the formation determinant for $H^{\cdot}$ specie) is:

$$\Delta_{H\cdot} = \begin{vmatrix} k_2a + 2k_4x & k_1a \\ -k_2a & k_1a \end{vmatrix} = 2k_1ak_2a + 2k_4xk_1a \tag{13}$$

$$[H\cdot]=\frac{2ak_1k_2a+2ak_4xk_1}{2k_4k_3a\sqrt{\frac{k_1}{k_4}a}}\cong\frac{2ak_1k_2a}{2k_4k_3a\sqrt{\frac{k_1}{k_4}a}}=\sqrt{\frac{k_1}{k_4}}\cdot\frac{k_2}{k_3}a^{1/2} \qquad (14)$$

Finally, the rate law,

$$r=k_2\sqrt{\frac{k_1}{k_4}}[CH_4]^{3/2} \qquad (15)$$

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

If we complicate the system by adding the reversible reactions, the decomposition of methane at 1600 degrees is described by the following mechanism[20]:

$$\begin{array}{ll}
CH_4 \xrightarrow{k_1} CH_3^{\cdot} + H^{\cdot} & k_1=14\ s^{-1} \\
H^{\cdot} + CH_4 \xrightarrow{k_2} CH_3^{\cdot} + H_2 & k_2=1.5*10^{12}\ L/mol\cdot s \\
H_2 + CH_3^{\cdot} \xrightarrow{k_{-2}} H^{\cdot} + CH_4 & k_{-2}=2.9*10^{10}\ L/mol\cdot s \\
CH_3^{\cdot} + CH_3^{\cdot} \xrightarrow{k_3} C_2H_6 & k_3=2*10^{13}\ L/mol\cdot s \\
C_2H_6 \xrightarrow{k_{-3}} CH_3^{\cdot} + CH_3^{\cdot} & k_{-3}=4.5*10^{4}\ s^{-1} \\
CH_3^{\cdot} + H^{\cdot} \xrightarrow{k_{-1}} CH_4 & k_{-1}=1.2*10^{13}\ L/mol\cdot s
\end{array} \qquad (16)$$

with the global reaction:

$$2CH_4 \rightarrow C_2H_6 + H_2 \qquad (17)$$

The flow graph for this mechanism is a perfect image of it (figure 3). To form this graph we neglect the step of interruption between the hydrogen and methyl radicals because it is insignificant in compression with those of methyl radicals:

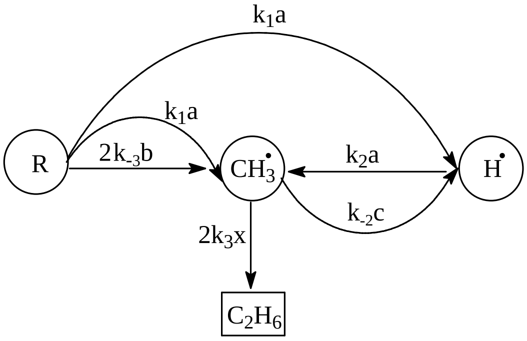

**Figure 3. Flow graph for methane pyrolysis**

where **R** is the impute node or source of the interested specie, radicals. We note with

$x=[CH_3^{\cdot}]$ $a=[CH_4]$ $b=[C_2H_6]$ $c=[H_2]$.

The main determinant is obtained by following the way from the radicals to the output node, the final product:

$$\Delta = k_2 a * 2k_3 x \,,$$

which is the consumption determinant because it refers to the consumption of the radicals species in favor of formations of the product.

The formation determinant for the $CH_3^{\cdot}$ species is equal with

$$\Delta_{CH_3^{\cdot}} = \Delta_x = k_2 a(2k_1 a + 2k_{-3} b) \tag{18}$$

which results from the gain of the formation flow graph which is formed by considering the specie $CH_3^{\cdot}$ as a target (figure 4):

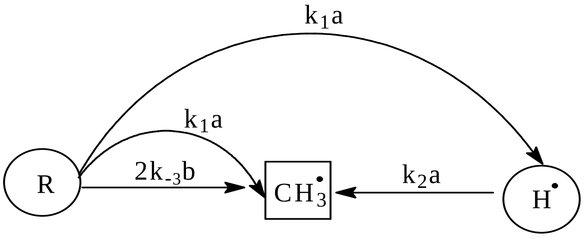

**Figure 4. The flow graph for $\Delta_{CH3}$**

Taking in account of Cramer's rule the concentration of methyl species is:

$$x = \frac{\Delta_x}{\Delta} = \frac{k_2 a(2k_1 a + 2k_{-3} b)}{k_2 a\ 2k_3 x} \qquad x = \left(\frac{k_1 a + k_{-3} b}{k_3}\right)^{1/2}$$

but we have already considered the QSSA valuable, then the concentration have richen to the equilibrium and in consequence we can neglect the term $k_1 a$.

$$x = \left(\frac{k_{-3} b}{k_3}\right)^{1/2} \tag{19}$$

In the same way we can draw the flow graph corresponding to the formation determinant of the hydrogen radical specie (figure 5):

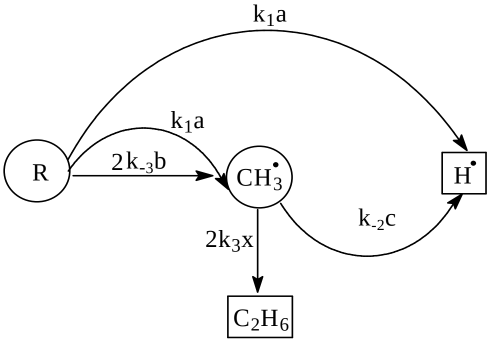

**Figure 5. The flow graph for $\Delta_H$**

The gain of the flow graph is:

$$\Delta_{H^{\cdot}} = 2k_1ak_{-2}c + 2k_{-3}bk_{-2}c + 2k_3xk_1a$$

$$[H^{\cdot}] = \frac{2k_{-2}c(k_1a + k_{-3}b) + 2k_3x\,k_1a}{2k_3x\,k_2a} = \frac{k_{-2}c\,k_{-3}b}{k_2a\,k_3x} + \frac{k_1}{k_2} \qquad (20)$$

To find the dependence of the methane concentration to time we have to write the differential equation:

$$\frac{d[CH_4]}{dt} = k_{-2}[CH_3^{\cdot}][H_2] + k_{-1}[H^{\cdot}][CH_3^{\cdot}] - k_2[H^{\cdot}][CH_4] - k_1[CH_4] \qquad (21)$$

$$\frac{d[CH_4]}{dt} = k_{-1}[H^{\cdot}][CH_3^{\cdot}] - 2k_1[CH_4] \qquad (22)$$

$$\frac{da}{dt} = 130.25 \cdot \frac{(C_{A0} - a)^2}{a} + 3.75 \cdot 10^{-3} \cdot (C_{A0} - a)^{1/2} - 2k_1a \qquad (23)$$

If the numerical integration is applied the profile methane concentration – time was obtained. If we consider the fact that in calculation of species concentrations we didn't take in evidence the reaction $H + CH_3 \rightarrow CH_4$, we'll make the correction with factor $1 + \frac{k_{-1}k_{-2}}{k_3k_2}\frac{c}{a} + \frac{2k_{-1}}{k_2}\frac{x}{a}$ which represent the error made in finding the value of [H] concentration, by not considering the reaction $H + CH_3 \rightarrow CH_4$.

The numerical integration and calculation of all concentrations species was made by a Matlab program which is presented in the following, considering the QSSA:

```
t=0:0.0001:0.03;h=0.0001;y=zeros(1,301);y(1)=1e-6;
for i=1:300
y(i+1)=y(i)+h*(130.25*((y(1)-y(i))^2)/y(i)+3.75e-3*((y(1)-
y(i))^0.5)-28*y(i));
end
w=1e-6-y;x=3.35e-5*(w.^0.5);u=3.24*1e-
7*((w.^1.5)./y)+9.333*1e-
12;d=x./y;e=1+16*d;v=u./e;z=zeros(1,301);z(1)=1e-6;
for i=1:300
z(i+1)=z(i)+h*((130.25*((z(1)-z(i))^2)/z(i)+3.75e-
3*((z(1)-z(i))^0.5))*e(i)-28*z(i));
end
figure plot(t,(z*1e7),'m')
hold on plot(t,(l*1e8),'m')
hold on   plot(t,(v*1e11),'m')
xlabel('t[s]')
ylabel('Methane,Methil,Hidrogen concentrations')
hold off
```

This profiles are comparable with those obtained by Skinner[20] solving with a Fortran programe the differential equations system, and not considering the QSSA.

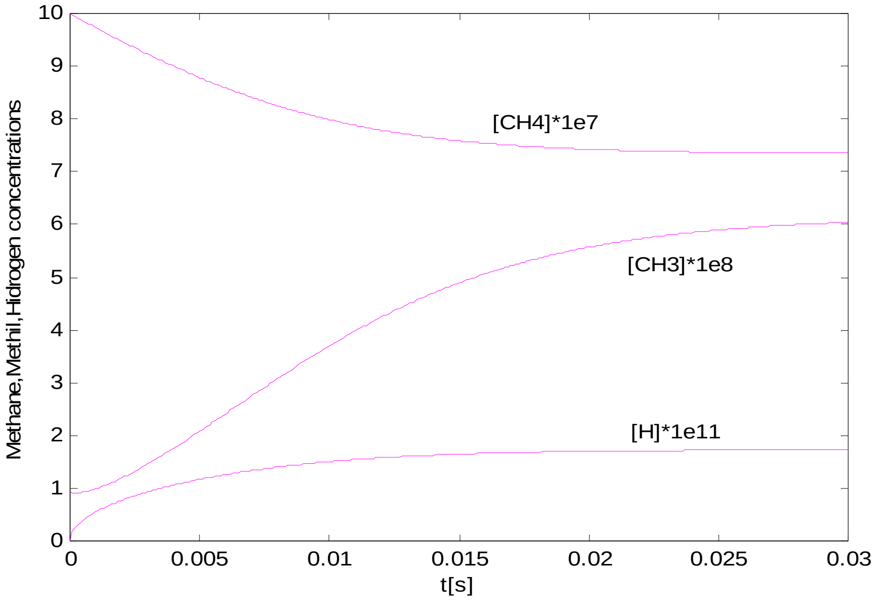

**Figure 6. Concentration dependence of time for methane pyrolysis**

## 4. THE PYROLISIS OF 1,3-DIPHENILPROPANE

The second example refers to 1,3-diphenilpropane pyrolysis and it's a kind of Rice-Herzfeld mechanism[21]:

$$Ph-CH_2-CH_2-CH_2-Ph \xrightarrow{k_I} Ph-CH_2^\bullet + Ph-CH_2-CH_2^\bullet$$ initiation

(a) $(R_1)$ $(R_2)$ (24)

$$Ph-CH_2^\bullet + Ph-CH_2-CH_2-CH_2-Ph \xrightarrow{k_H} Ph-CH_3 + Ph-CH^\bullet-CH_2-CH_2-Ph$$

$(R_1)$ $(R_3)$ (25)

$$Ph-CH^\bullet-CH_2-CH_2-Ph \xrightarrow{k_\beta} Ph-CH_2^\bullet + Ph-CH=CH_2 \quad (26)$$

$$R_3 + R_3 \xrightarrow{k_{T_1}} Product_2$$ termination (27)

$$R_3 + R_1 \xrightarrow{k_{T_2}} Product_1$$ termination (28)

$$R_1 + R_1 \xrightarrow{k_{T_3}} Product_3$$ termination (29)

The representative flow graph (figure 7) for the mechanism is as follows:

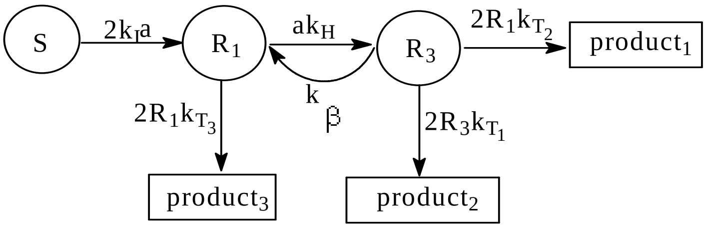

**Figure 7. Flow graph for 1,3-diphenilpropane pyrolysis**

the rate law is:

$$r = ak_H R_1 \qquad (30)$$

The mechanism system is as follows:

$$\begin{array}{cc} & \begin{array}{cc} R_1 & R_3 \end{array} \qquad\qquad\qquad\qquad a \\ \begin{array}{c} R_1 \\ \\ R_3 \end{array} & \left|\begin{array}{cc} ak_H+2R_1k_{T_3} & -k_\beta \\ & \\ -ak_H & 2R_1k_{T_2}+2R_3k_{T_1}+k_\beta \end{array}\right| \cdot \left(\begin{array}{c} R_1 \\ \\ R_3 \end{array}\right) = \left|\begin{array}{c} 2k_1a \\ \\ 0 \end{array}\right| \end{array} \qquad (31)$$

$$\begin{aligned} \Delta &= (ak_H + 2R_1k_{T_3})(2R_1k_{T_2} + 2R_3k_{T_1} + k_\beta) - ak_Hk_\beta = \\ &= ak_H(2R_1k_{T_2} + 2R_3k_{T_1}) + 2R_1k_{T_3}(2R_1k_{T_2} + 2R_3k_{T_1} + k_\beta) \end{aligned} \qquad (32)$$

The value of this determinant (the global consumption radical) is also equal with the global gain of flow graph without considering the reactant (the input node) following the given rules of the flow graphs.

Taking in account that: $2R_1k_{T_2} + 2R_3k_{T_1} << k_\beta$

$$\Delta = ak_H(2R_1k_{T_2} + 2R_3k_{T_1}) + 2R_1k_{T_3}k_\beta \qquad (33)$$

Also, using the same proprieties of the flow graphs (following the branch way, starting from the reactant, to the aimed radical) we obtain:

$$\Delta_{R_1} = a2k_Ik_\beta \quad \text{and} \quad \Delta_{R_3} = 2ak_Iak_H \qquad (34)$$

According with Cramer's method, we have:

$$\frac{R_3}{R_1} = \frac{\Delta R_3}{\Delta R_1} = \frac{ak_H}{k_\beta} \qquad R_3 = \left(\frac{ak_H}{k_\beta}\right)R_1$$

$$R_1 = \frac{\Delta R_1}{\Delta} = \frac{2ak_I \cdot k_\beta}{2ak_HR_1k_{T_2} + 2ak_Hk_{T_1}R_3 + 2R_1k_{T_3}k_\beta}$$

$$R_1^2 = \frac{a \cdot k_I}{\frac{ak_H}{k_\beta} \cdot k_{T_2} + \left(\frac{ak_H}{k_\beta}\right)^2 \cdot k_{T_1} + k_{T_3}}$$

$$R_1 = \left(\frac{ak_I}{\frac{ak_H}{k_\beta} \cdot k_{T_2} + \left(\frac{ak_H}{k_\beta}\right)^2 \cdot k_{T_1} + k_{T_3}}\right)^{1/2} \tag{35}$$

knowing that $r = ak_H R_1$ it results

$$r = ak_H \left(\frac{ak_I}{\frac{ak_H}{k_\beta} \cdot k_{T_2} + \left(\frac{ak_H}{k_\beta}\right)^2 \cdot k_{T_1} + k_{T_3}}\right)^{1/2} \tag{36}$$

Equation (36) is the same with that one obtained by applying quasi-steady state approximation (QSSA)[22,23] and long-chain approximation (LCA)[24].

## 5. THE PYROLISIS OF PROPANE

An example illustrating a very complex mechanism is the one referring at thermal decomposition of propane[25]. Homogenous pyrolysis of propane between 1050 – 1250 K has been chosen as an example because every proposed mechanism in last few years[26-28] are obeying the mechanism formed from eleven reactions, proposed by Lifshitz and Frenklach[29], although there are some inconcordances by means of rate constants values for some reaction

The described mechanism is as follows:

$C_3H_8 \xrightarrow{k_1} CH_3^\bullet + C_2H_5^\bullet$ $k_1 = 1.168\ s^{-1}$

$CH_3^\bullet + C_3H_8 \xrightarrow{K_2} CH_4 + i-C_3H_7^\bullet$ $k_2 = 10^7$ L/mol·s

$CH_3^\bullet + C_3H_8 \xrightarrow{K_3} CH_4 + n-C_3H_7^\bullet$ $k_3 = 1.21 \times 10^7$ L/mol·s

$H^\bullet + C_3H_8 \xrightarrow{k_4} H_2 + i-C_3H_7^\bullet$ $k_4 = 7.31 \times 10^8$ L/mol·s

$H^\bullet + C_3H_8 \xrightarrow{k_5} H_2 + n-C_3H_7^\bullet$ $k_5 = 8.84 \times 10^8$ L/mol·s

$i-C_3H_7^\bullet \xrightarrow{k_6} C_2H_4 + CH_3^\bullet$ $k_6 = 1.35 \times 10^5\ s^{-1}$ (37)

$n-C_3H_7^\bullet \xrightarrow{k_7} C_2H_4 + CH_3^\bullet$ $k_7 = 1.61 \times 10^7\ s^{-1}$

$i-C_3H_7^\bullet \xrightarrow{k_8} C_3H_6 + H^\bullet$ $k_8 = 1.23 \times 10^6\ s^{-1}$

$n-C_3H_7^\bullet \xrightarrow{k_9} C_3H_6 + H^\bullet$ $k_9 = 1.81 \times 10^6\ s^{-1}$

$C_2H_5^{\bullet} \xrightarrow{k_{10}} C_2H_4 + H^{\bullet}$ $k_{10} = 2.58 \times 10^5\ s^{-1}$

$CH_3^{\bullet} + CH_3^{\bullet} \xrightarrow{k_{11}} C_2H_6$ $k_{11} = 9.00 \times 10^9$ L/mol·s

For such a mechanism, the calculation is very difficult and it takes a long time and attention. That’s why we appeal to the method of flow graph.

The flow graph (figure 8) is as follows:

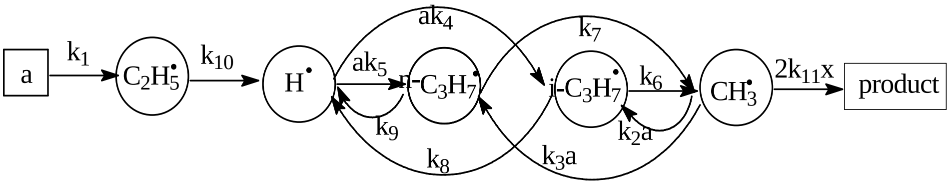

**Figure 8. Flow graph for propane pyrolysis**

we note: a = [$C_3H_8$] and $x = [CH_3^{\bullet}]$; Using the proprieties of the flow graphs we obtain:

$$\Delta = k_{10}ak_4k_6k_9 2k_{11}x + k_{10}ak_5k_7 2k_{11}xk_8 + k_{10}ak_4k_6 2k_{11}xk_7 + k_{10}ak_5k_7k_6 2k_{11}x = 2k_{10}k_{11}xa[k_4k_6(k_7+k_9)+k_5k_7(k_6+k_8)] \quad (38)$$

$$\Delta_x = 2a^2k_1k_{10}[k_4k_6(k_7+k_9)+k_5k_7(k_6+k_8)] \quad (39)$$

$$\Delta_{H\cdot} = 2ak_1k_{10}[k_8k_7k_2a + k_8k_2ak_9 + k_3ak_9k_8 + k_3ak_9k_6 + k_{11}x(k_6k_7 + k_7k_8 + k_9k_6 + k_8k_9)] \quad (40)$$

$$\Delta_{C_2H_5\cdot} = 2a^2k_1k_{11}x(k_5k_6k_7 + k_4k_6k_7 + k_5k_7k_8 + k_4k_6k_9) \quad (41)$$

$$\Delta_{i-C_3H_7\cdot} = 2a^2k_1k_4k_{10}[k_3ak_9 + k_2ak_9 + k_2ak_7 + k_{11}x(k_7+k_9)] \quad (42)$$

$$\Delta_{n-C_3H_7\cdot} = 2a^2k_1k_5k_{10}[k_2ak_8 + k_3ak_8 + k_3ak_6 + k_{11}x(k_6+k_8)] \quad (43)$$

Using the Cramer’s rules we obatin:

$$[CH_3\cdot] = \frac{\Delta_x}{\Delta} \quad (44)$$

$$[H\cdot] = \frac{\Delta_{H\cdot}}{\Delta} \quad (45)$$

$$[C_2H_5\cdot] = \frac{\Delta_{C_2H_5\cdot}}{\Delta} \quad (46)$$

$$[i-C_3H_7\cdot] = \frac{\Delta_{i-C_3H_7\cdot}}{\Delta} \quad (47)$$

$$[n-C_3H_7\cdot]=\frac{\Delta_{n-C_3H_7\cdot}}{\Delta} \quad (48)$$

with the rate law:

$$-\frac{d[C_3H_8]}{dt}=k_1[C_3H_8]+(k_2+k_3)[CH_3^{\cdot}][C_3H_8]+(k_4+k_5)[H^{\cdot}][C_3H_8] \quad (49)$$

Using these equations we obtain:

$$[CH_3^{\cdot}]=1.14*10^{-5}*\sqrt{a}\ \ ,\ [H^{\cdot}]=1.346*10^{-9}*(10^2*\sqrt{a}+1)\ ,[C_2H_5^{\cdot}]=4.535*10^{-6}*a$$
$$[i-C_3H_7^{\cdot}]=7.23*10^{-7}*a*(110*\sqrt{a}+1) \quad (50)$$
$$[n-C_3H_7^{\cdot}]=6.68*10^{-8}*a*(205.5*\sqrt{a}+1)$$

and for initial concentration of propane by $10^{-6}$ mol/l we obtain:

$[CH_3]=1.14*10^{-8}$;$[H]=1.485*10^{-9}$; $[C_2H_5]=4.535*10^{-12}$; (51)
$[i\text{-}C_3H_7]=8.025*10^{-13}$; $[n\text{-}C_3H_7]=8.056*10^{-14}$;

The program in Matlab which solves the differential system without any approximation (QSSA) using the numerical methods is:

```
t=0:1e-7:0.03;h=1e-7;
k1=1.168;k2=1e7;k3=1.21e7;k4=7.31e8;k5=8.84e8;k6=1.35e5;
k7=1.61e7;
k8=1.23e6;k9=1.81e6;k10=2.58e5;k11=9e9;
y=zeros(1,(3e5+1));z=zeros(1,(3e5+1));w=zeros(1,(3e5+1));u=z
eros(1,(3e5+1)); v=zeros(1,(3e5+1));r=zeros(1,(3e5+1));
y(1)=1e-6;z(1)=0;w(1)=0;u(1)=0;v(1)=0;r(1)=0;
for i=1:3e5
   y(i+1)=y(i)-
h*(k1*y(i)+(k2+k3)*r(i)*y(i)+(k4+k5)*y(i)*w(i));
   z(i+1)=z(i)+h*(k1*y(i)-k10*z(i));
   w(i+1)=w(i)+h*(k8*v(i)+k9*u(i)+k10*z(i)-
(k4+k5)*y(i)*w(i));
   u(i+1)=u(i)+h*(k3*r(i)*y(i)+k5*w(i)*y(i)-(k7+k9)*u(i));
   v(i+1)=v(i)+h*(k2*r(i)*y(i)+k4*w(i)*y(i)-(k6+k8)*v(i));
   r(i+1)=r(i)+h*(k1*y(i)+k6*v(i)+k7*u(i)-
(k2+k3)*y(i)*r(i)-k11*r(i)*r(i));
end
figure
plot(t,(y*1e7))
hold on
plot(t,(z*1e12))
hold on
plot(t,(w*1e9))
hold on
plot(t,(u*1e14))
hold on
plot(t,(v*1e13))
hold on
```

```
plot(t,(r*1e8))
xlabel('t[s]') ylabel('Propane,Ethil,Hidrogen,n-Propil,
i-Propil,Methil concentrations')
hold off
```

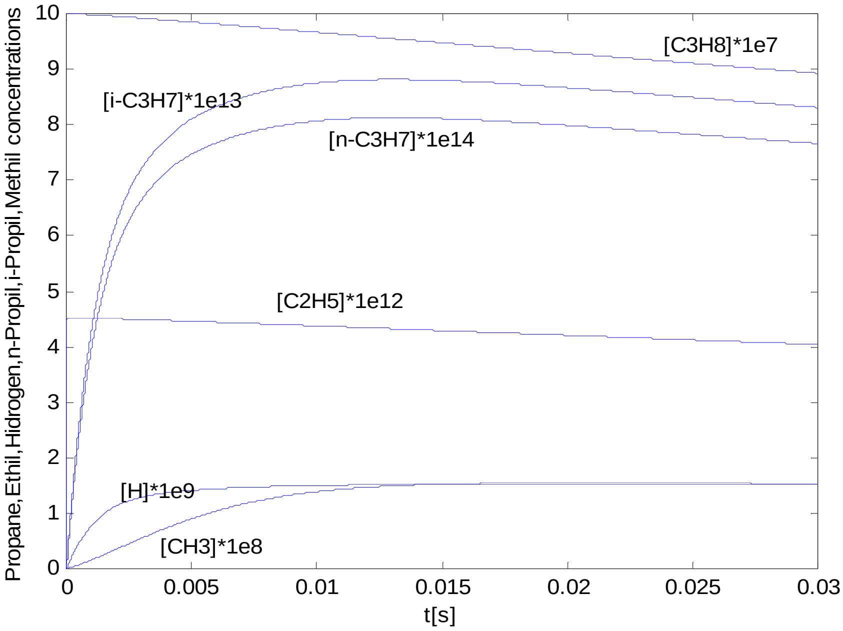

**Figure 9. Concentration dependence of time for propane pyrolysis**

It is observed that the stationary concentrations obtained are approximately the same with those obtained with graph theory using QSSA approximation.

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