



## KINETIC GRAPHS AS A USEFUL TOOL FOR THE KINETIC DESCRIPTION OF CATALYTIC AND CHAIN REACTIONS

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Using the kinetic graphs method, the rate equations for some heterogeneous catalytic, homogeneous catalytic, enzyme and chain reactions were derived. The results are in good agreement with those obtained using the quasi-steady state approximation.

### INTRODUCTION

The formal-kinetic treatment of complex reactions benefits mainly by the quasi-steady state approximation which is used in order to eliminate the unknown concentrations of intermediates expressing them as functions of the known concentrations of reactants and products. As an alternative procedure, in the last decades, formal kinetics uses the graph theory which permits to obtain results identical with those based on the quasi-steadystate approximation. Sometimes this alternative method uses more simple calculations and with more general results. This note aims to present some results obtained by using graphs in order to derive rate equations concerning heterogeneous and homogeneous catalytic reactions, enzyme and chain reactions.<sup>1-6</sup> We are going to describe linear systems with one active center in each elementary step. General information and definitions concerning application of graphs in chemical kinetics can be found in our previous papers<sup>1</sup> as well as in other literature sources.<sup>7-9</sup>

In the following we are going to present, using graph theory, only catalytic and chain reactions with straight chains, which by definition suppose linear mechanisms.

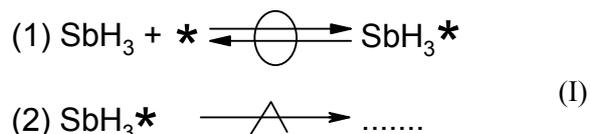
Considering a stage,  $s$  (ensemble of two reversible steps which occur with the participation

of the active centers  $X_s$  and  $X_{-s}$ ), the reaction rate is given by the relation:

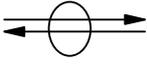
$$r = \omega_s \frac{D_s}{\Sigma D_s} - \omega_{-s} \frac{D_{-s}}{\Sigma D_s} \quad (1)$$

where  $D_s$  is the basic determinant corresponding to the vertex  $s$  from the representative graph of the reaction mechanism and  $\omega_s$  is the frequency of step  $s$  (the rate of the step divided by the concentration of active center attending in it). Actually in its general form, relation (1) should contain as a factor the total concentration of the active centers. For heterogeneous catalytic reactions where the concentrations are expressed in degrees of coverage the supplementary factor equals unity.

The first example of heterogeneous catalytic reaction that we mention is the decomposition of stibine on antimony surfaces.<sup>1,10</sup> The reaction can be described by the following two steps sequence:



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where the first stage is at equilibrium, , and the second step is rate determining, . The symbol \* means a surface center.

The representative graph of the two step sequence (I) is given in Fig. 1.

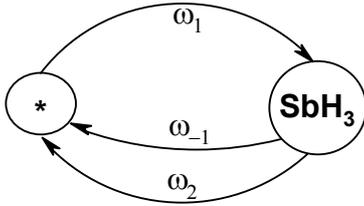


Fig. 1

The basic determinants are:

$$D_* = \omega_{-1} + \omega_2$$

$$D_{SbH_3} = \omega_1$$

$$\Sigma D_s = \omega_1 + \omega_{-1} + \omega_2$$

By introducing these results in formula (1) it turns out that:

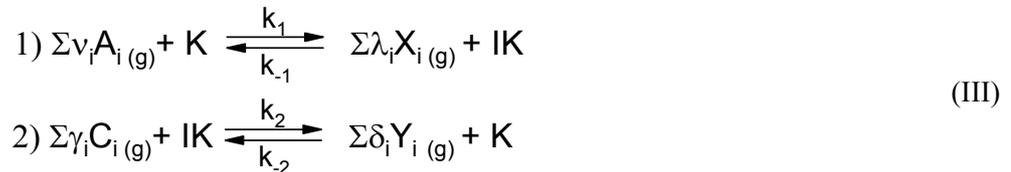
$$r = \frac{\omega_1(\omega_{-1} + \omega_2) - \omega_1\omega_{-1}}{\omega_1 + \omega_{-1} + \omega_2} \quad (2)$$

Taking into account that the second step is rate determining it follows that:

$$r = \frac{\omega_1\omega_2}{\omega_1 + \omega_{-1}} \quad (3)$$



where  $\nu_i, \gamma_i, \lambda_i$  and  $\delta_i$  are stoichiometric coefficients which occurs through the sequence:



where the symbol  $\Sigma$  means sum and IK is a reaction intermediate, will be considered.

The frequencies of the four steps involved in sequence (III) are obviously given by:

$$r = \frac{k_1 k_2 P_{NH_3}}{k_{-1} + k_1 P_{NH_3}} \quad (4)$$

and

$$r = \frac{k_2 K_1 P_{SbH_3}}{1 + K_1 P_{SbH_3}} \quad (5)$$

where  $k_i$  are rate constants and  $K_1$  is the equilibrium constant of the first stage in sequence (I). Relation (5) is equivalent to:

$$r \propto P_{SbH_3}^n \quad (6)$$

with  $0 < n < 1$

which is experimentally verified.<sup>11</sup>

Similar treatments were applied for other monoroute heterogeneous catalytic reactions like dehydrogenation of methylcyclohexane on Pt/Al<sub>2</sub>O<sub>3</sub>,<sup>12</sup> hydrogenolysis of ethane,<sup>13</sup> coal gasification,<sup>14</sup> dehydrogenation of secondary alcohols.<sup>15</sup> For the formal kinetic treatment of three step monoroute catalytic reactions the method of King and Altman should be mentioned.<sup>16</sup>

Among the multi route heterogeneous catalytic reactions we mention the interaction between the nitrogen oxides and carbon monoxide on silver (two route reaction)<sup>1,8,14</sup> and the transformation of n-hexane on supported platinum.<sup>17</sup>

In the following a two step model of the generalized catalytic reaction.

$$\begin{aligned} \omega_1 &= k_1 \Pi P_{A_i}^{\nu_i} \\ \omega_2 &= k_2 \Pi P_{C_i}^{\gamma_i} \\ \omega_{-1} &= k_{-1} \Pi P_{X_i}^{\lambda_i} \\ \omega_{-2} &= k_{-2} \Pi P_{Y_i}^{\delta_i} \end{aligned} \quad (7)$$

where the symbol  $\Pi$  means product.

The representative graph for the two-step sequence (III) is:

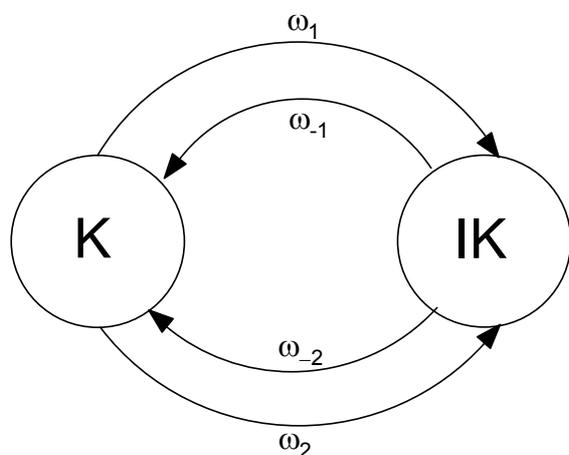


Fig. 2

and the reaction rate according to the general formula (1)

$$r = \frac{k_1 k_2 P_A P_C - k_{-1} k_{-2} P_X P_Y}{k_1 P_A + k_{-1} P_X + k_2 P_C + k_{-2} P_Y} \quad (8)$$

where

$$\begin{aligned} P_A &= \Pi P_{A_i}^{v_i} \\ P_C &= \Pi P_{C_i}^{z_i} \\ P_X &= \Pi P_{X_i}^{\lambda_i} \\ P_Y &= \Pi P_{Y_i}^{\delta_i} \end{aligned} \quad (9)$$

Among the chain reactions with straight chains whose propagation steps were treated by means of kinetic graphs, the rate of hydrobromic acid formation from elements could be mentioned. For the detailed calculations the general formula of the reaction rate was used in the form:

$$r = \frac{\sum_i \omega_i D_i}{\sum_i D_i} \sum_k c_k \quad (10)$$

where  $D_i$  is the basic determinant of the vertex  $i$  from the representative graph,  $\omega_i$  is the frequency of the propagation step  $i$  and  $c_k$  is the concentration of the active center attending in it.

For the generation of hydrobromic acid, the particular form of equation (10) is:

$$r = \frac{k_2 k_3 c_{H_2} c_{Br_2}}{k_2 c_{H_2} + k_{-2} c_{HBr} + k_3 c_{Br_2}} (c_{Br} + c_H) \quad (11)$$

where  $k_2$  and  $k_{-2}$  are the rate constants for the reversible propagation step,  $k_3$  is the rate constant for the irreversible propagation step and the symbol  $c$  is used for concentration.

As the bromine atoms are the rate determining active centers<sup>18</sup>  $c_{Br} > c_H$  and

$$r = \frac{k_2 k_3 c_{H_2} c_{Br_2}}{k_2 c_{H_2} + k_{-2} c_{HBr} + k_3 c_{Br_2}} c_{Br} \quad (12)$$

In order to eliminate the unknown concentration of the bromine atoms one has to take into account the fact that for straight chain reactions the rate of chain initiation equals the rate of the termination step. Under such conditions from relation (12) one obtains:

$$r = \frac{\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}} k_2 k_3 c_{H_2} c_{Br_2} (c_{Br_2})^{\frac{1}{2}}}{1 + \frac{k_2 c_{H_2}}{k_3 c_{Br_2}} + \frac{k_{-2} c_{HBr}}{k_3 c_{Br_2}}} \quad (13)$$

As<sup>10</sup>  $E_2 = 17.6$  kcal.mole<sup>-1</sup> and  $E_3 = 1.2$  kcal.mole<sup>-1</sup>,  $E_i$  being activation energy,

$$\frac{k_2 c_{H_2}}{k_3 c_{Br_2}} \ll 1$$

equation (13) takes the simple form:

$$\frac{dc_{HBr}}{dt} = \frac{2 \left(\frac{k_1}{k_2}\right)^{\frac{1}{2}} k_2 c_{H_2} c_{Br_2}^{\frac{1}{2}}}{1 + \frac{k_{-2} c_{HBr}}{k_3 c_{Br_2}}} \quad (14)$$

which is identical with that obtained by using the quasi-steady-state approximation<sup>19-21</sup> as well as with the equation obtained experimentally by Bodenstein and Lind.<sup>22</sup>

Among the gas-phase catalytic homogeneous reactions treated by means of graphs the reaction between nitric oxide and chlorine catalysed by bromine as well as the decomposition of acetaldehyde catalysed by iodine should be mentioned.<sup>6</sup>

Our research comprised also some models for irreversible inactivation of catalase in the enzyme

decomposition of hydrogen peroxide as well as their treatment by means of graphs.<sup>4</sup> The dependence of reaction rate on enzyme and substrate concentrations was investigated.

### CONCLUSIONS

As an alternative to the quasi-steady state approximation (QSSA) the graph method proves to be a powerful tool for formal kinetic analysis.

The rate equations obtained by the graph method for some heterogeneous catalytic, homogeneous gas-phase catalytic, enzyme and straight chain reactions are identical with those obtained by using QSSA.

Actually the graph method is an exact one and sometimes leads to more general results in comparison with the QSSA.

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