

APPLICATIONS OF AN ALGORITHM TO DERIVE RATE EQUATIONS BY MEANS OF KINETIC GRAPHS

Eugen I. SEGAL*

Department of Physical Chemistry, Faculty of Chemistry,
University of Bucharest, Bulevardul Elisabeta 4-12, Bucharest, Roumania

Received February 27, 2009

The paper deals with some applications of an algorithm to derive rate equations by means of graph theory. Gas phase reactions as well as heterogeneous catalytic reactions were considered. The resulted rate equations agree satisfactorily with those obtained using the quasisteady state approximation.

INTRODUCTION

In a series of previous articles and notes¹⁻⁶ using an algorithm based on graph theory we derived rate equations for two and many steps thermal, catalytic and chain reactions. This work continues the formal-kinetic analysis by applying the same algorithm to other reactions. We shall consider linear mechanisms.

For a reaction which occurs through the stage s (the ensemble of the two reversible steps which occur with the participation of the centers X_s and X_{-s}), the reaction rate is given by the formula¹:

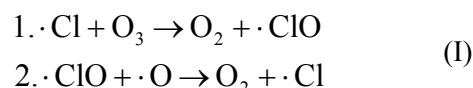
$$r = \omega_s \frac{D_s}{\sum D_s} - \omega_{-s} \frac{D_{-s}}{\sum D_s} \quad (1)$$

where D_s is the basic determinant of the vertex i from the representative graph of the reaction and ω_s is the frequency of the step s (the rate of the step divided by the concentration of active centers attending it, X_s). Concerning the derivation of formula(1) as well as the graphs and their applications in chemical kinetics the reader is sent to some literature sources.⁷⁻⁹

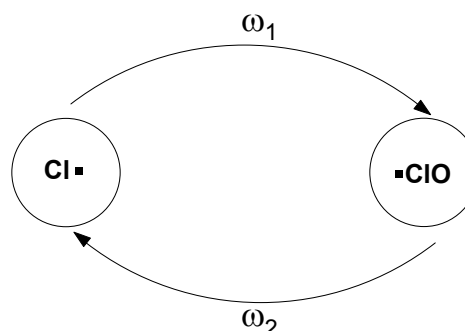
In the following, the formal kinetics of some relatively simple reactions treated by means of graphs and the corresponding derived rate equations are presented.

DECOMPOSITION OF OZONE CATALYZED BY ATOMIC CHLORINE

For the reaction (1) which takes place in stratosphere the following two step mechanism was suggested:¹⁰



The associated graph has the simple form:



with the basic determinants:

$$\begin{aligned} D_{Cl} &= \omega_2 = k_2 C_{\text{O}} \\ D_{ClO} &= \omega_1 = k_1 C_{\text{O}_3} \end{aligned} \quad (2)$$

The application of formula (1) leads to the following expression for the reaction rate:

$$r = \frac{k_1 k_2 C_{\text{O}} C_{\text{O}_3}}{k_1 C_{\text{O}_3} + k_2 C_{\text{O}}} C_L \quad (3)$$

with

$$C_L = C_{Cl} + C_{ClO} \quad (4)$$

Relation (3) is identical with the one obtained by means of the quasi steady state approximation¹⁰.

* Corresponding author: esegal@gw-chimie.math.unibuc.ro

THE REACTION BETWEEN NITRIC OXIDE AND CHLORINE CATALYSED BY BROMINE

As shown by Kiss¹¹ the rate equation for the reaction

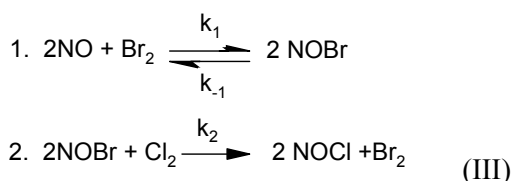


if it occurs in the presence of bromine is¹²:

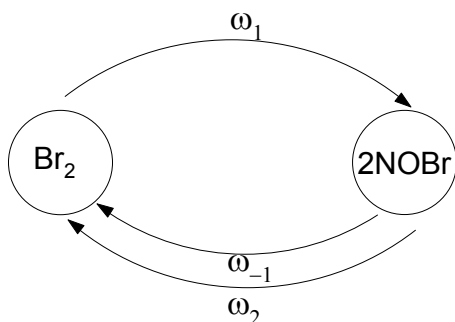
$$\frac{dC_{\text{NOCl}}}{dt} = kC_{\text{NO}}^2C_{\text{Cl}_2} + k_c C_{\text{NO}}^2C_{\text{Cl}_2}C_{\text{Br}_2} \quad (\text{5})$$

where k_c is the catalytic rate constant.

For the catalytic reaction the following two-step mechanism was suggested¹¹:



with the following associated graph:



where

$$\begin{aligned} \omega_1 &= k_1 C_{\text{NO}}^2 \\ \omega_{-1} &= k_{-1} \\ \omega_2 &= k_2 C_{\text{Cl}_2} \end{aligned} \quad (\text{6})$$

and

$$\begin{aligned} D_{\text{Br}_2} &= \omega_{-1} + \omega_2 \\ D_{\text{NOBr}} &= \omega_{-1} \end{aligned} \quad (\text{7})$$

Formula (1) taking into account relations (6) and (7) takes the form:

$$r_c = \frac{k_1 k_2 C_{\text{NO}}^2 C_{\text{Cl}_2}}{k_{-1} + k_2 C_{\text{Cl}_2} + k_1 C_{\text{NO}}^2} C_{\text{Br}_2} \quad (\text{8})$$

Taking into account that step 2 is a limiting step and for $k_1 C_{\text{NO}}^2 < k_{-1}$ relation (8) reduces to the second term of relation (5) with

$$k_c = \frac{k_1 k_2}{k_{-1}}$$

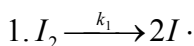
obtained by using the quasi steady state approximation and verified by experience.

The application of formula (1) needs linear mechanisms. Apparently the second step of sequence (3) is not linear. The problem could be solved by formally considering 2NOBr as a unique molecular formation $(\text{NOBr})_2$ which acts as intermediate.

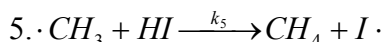
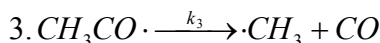
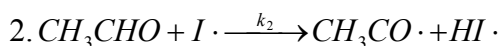
THE CATALYTIC DECOMPOSITION OF ACETALDEHYDE

The reaction occurs in the presence of iodine which acts as a catalyst according to the following mechanism:

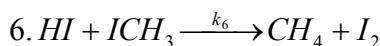
Initiation



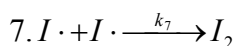
Propagation



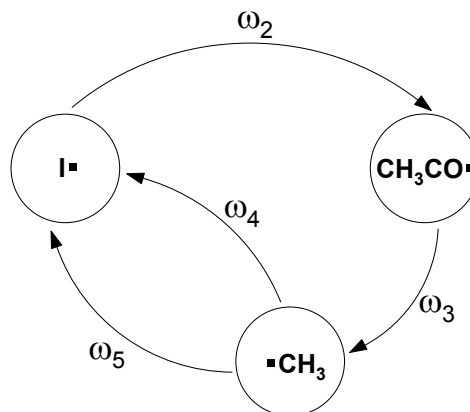
Catalyst regeneration



Termination



with the following associated graph:



and corresponding basic determinants:

$$\begin{aligned} D_I &= \omega_3(\omega_4 + \omega_5) \\ D_{CH_3CO} &= \omega_2(\omega_4 + \omega_5) \\ D_{CH_3} &= \omega_2\omega_3 \end{aligned} \quad (9)$$

The application of formula (1) to the propagation steps taking into account relations (9) gives the following rate equation:

$$r = \frac{k_2 k_3 (k_4 C_{I_2} + k_5 C_{HI}) C_{CH_3CHO} (C_I + C_{CH_3CO} + C_{CH_3})}{k_3 (k_4 C_{I_2} + k_5 C_{HI}) + k_2 k_3 C_{CH_3CHO} + k_2 (k_4 C_{I_2} + k_5 C_{HI}) C_{CH_3CHO}} \quad (10)$$

For $C_I < C_{CH_3CO}, C_{CH_3}$ equation (10) after simple transformations takes the form:

$$r = \frac{k_2 C_{CH_3CHO} C_I}{1 + \frac{k_2}{k_4 C_{I_2} + k_5 C_{HI}} C_{CH_3CHO} + \frac{k_2 C_{CH_3CHO}}{k_3}} \quad (11)$$

Taking into account this last result equation (11) turns into:

$$r = k_2 \left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} C_{I_2}^{\frac{1}{2}} C_{CH_3CHO} \quad (12)$$

which is identical with that obtained by using the quasisteady state approximation¹³.

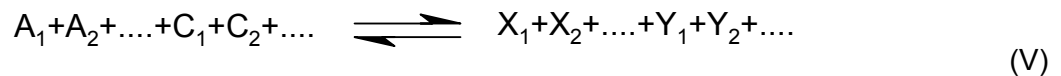
which if $k_2 < k_3, k_4, k_5$ reduces to:

$$r = k_2 C_{CH_3CHO} C_I.$$

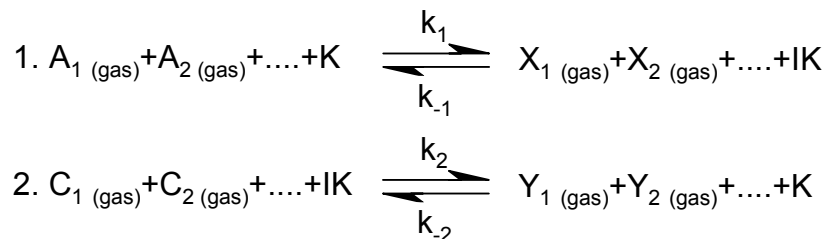
From the equality between the rates of initiation and termination one obtains:

$$C_I = k_2 \left(\frac{k_1}{k_7}\right)^{\frac{1}{2}} C_{I_2}^{\frac{1}{2}}$$

Let us consider the reaction:^{14,15}



which occurs according to the two stage mechanism:

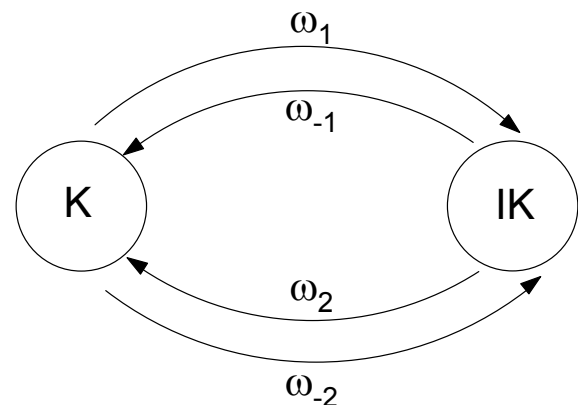


where K is the catalyst and IK the reaction intermediate.

The frequencies $\omega_1, \omega_{-1}, \omega_2, \omega_{-2}$ of the two stages of reaction (V) are given by the relations:

$$\begin{aligned} \omega_1 &= k_1 P_{A_1} P_{A_2} \dots P_{A_i} \\ \omega_{-1} &= k_{-1} P_{X_1} P_{X_2} \dots P_{X_i} \\ \omega_2 &= k_2 P_{C_1} P_{C_2} \dots P_{C_i} \\ \omega_{-2} &= k_{-2} P_{Y_1} P_{Y_2} \dots P_{Y_i} \end{aligned} \quad (13)$$

The graph associated to reaction (V) which occurs through stages 1 and 2 is:



and the reaction rate according to formula (1) is given by:

$$r = \frac{k_1 k_2 P_A P_C - k_{-1} k_{-2} P_X P_Y}{k_1 P_A + k_{-1} P_X + k_2 P_C + k_{-2} P_Y} \quad (14)$$

where

$$\begin{aligned} P_A &= P_{A_1} P_{A_2} \dots P_{A_i} \\ P_C &= P_{C_1} P_{C_2} \dots P_{C_i} \\ P_X &= P_{X_1} P_{X_2} \dots P_{X_i} \\ P_Y &= P_{Y_1} P_{Y_2} \dots P_{Y_i} \end{aligned} \quad (15)$$

CONCLUSIONS

For the linear mechanisms the formal kinetic analysis by means of graphs leads to results equivalent to those obtained using the quasisteady state approximation.

For some cases the use of graphs is simpler than the quasisteady state approximation.

The algorithm based on graphs in order to derive rate equation seems to lead to more general results.

REFERENCES

1. E. Segal, *Progress in Catalysis*, **1997**, 6, 135.
2. E. Segal, *Progress in Catalysis*, **1998**, 7, 43.
3. A. Răducan, D. Oancea and E. Segal, *Progress in Catalysis*, **1998**, 7, 139.
4. E. Segal, *Analele Universității București, Chimie*, **2002**, 11, 139.
5. E. Segal, *Analele Universității București, Chimie*, **2002**, 11, 147.
6. E. Segal, *Analele Universității București, Chimie*, **2003**, 12, 257.
7. E.I. King and C. Altman, *J. Phys. Chem.*, **1956**, 60, 1375.
8. M.V. Volkenstein and B.N. Goldstein, *Doklady. Akad. Nauk SSSR*, 1966, 170.
9. V.A. Evstigneev and G.S. Yablonskii, *Kinetika i Kataliz*, **1979**, 20, 1549.
10. Michel Boudart and G. Djega-Mariadassou, "Kinetics of heterogeneous catalytic reactions, Princeton University Press", Princeton, N.J., **1984**, p. 27-28.
11. A. von Kiss, *Rec. Trav. Chim.*, **1923**, 42, 112; **1924**, 43, 68.
12. K. J. Laidler, "Chemical kinetics", McGraw-Hill, London, **1965**, p. 445.
13. V. Isac and N. Hurduc, "Chimie fizică. CINETICĂ CHIMICĂ ȘI CATALIZĂ". Editura Știința, Chișinău, **1994**, p. 304-306.
14. S.L. Kiperman, "Vvedenie V Kinetiku Gheteroghennikh Katalititceskikh Reaktzii", Izdatelstvo Nauka, Moskva, **1964**, p. 157.
15. M.I. Temkin, *J. Fiz. Khim.*, **1957**, 31, 3.