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Dedicated to Professor Victor-Emanuel Sahini on the occasion of his 85th anniversary

KINETIC ANALYSIS OF A MULTIROUTE REACTION BY MEANS OF GRAPHS

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The paper is dedicated to a complete analysis of the kinetics of a model multiroute system of elementary steps and stages. For the representative graph the kinetic characteristic, conjugation parameter and basic determinants were calculated. The obtained results allow a correct description of the considered system.

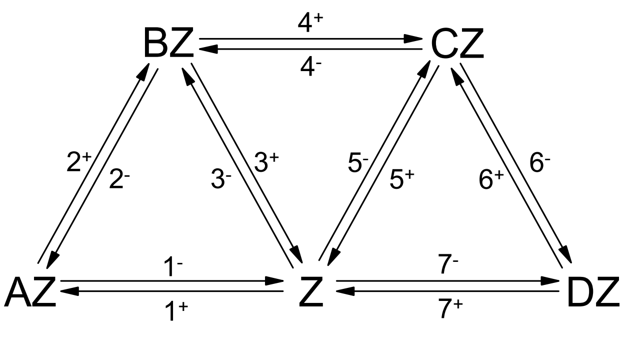
INTRODUCTION

Following our work concerning kinetics of many route reactions using graphs,[1] this note is dedicated to an attempt to a formal kinetic treatment of the following model system of seven stages:[2]

1. $A+Z \leftrightarrows AZ$
2. $AZ \leftrightarrows BZ$
3. $BZ \leftrightarrows B+Z$
4. $BZ \leftrightarrows CZ$ (I)
5. $CZ \leftrightarrows C+Z$
6. $CZ \leftrightarrows DZ$
7. $DZ \leftrightarrows D+Z$

with three routes.

The corresponding graph is:



One can easily see on it the three cycles corresponding to the reaction routes.

For the kinetic analysis the following formula

$$r_s = \frac{\sum_{i=1}^{M} \Omega_i P_i}{D} \tag{1}$$

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was used. In formula (1) r_s is the rate of an elementary step in the multi route reaction, M is the number of cycles in which the step s attends, Ω_i is the cyclic characteristic of cycle *i* given by:

$$\Omega_i = \prod{}_{\upsilon}\omega\ (\upsilon) - \prod{}_{\upsilon}\omega^{-}(\upsilon) \qquad (2)$$

υ is the number of arcs from the cycle i, ω is the frequency of a linear step, P_i is the conjugation parameter of the cycle *i* given by

$$P = \sum_{H} \omega(H) \qquad (3)$$

and H is the number of cycles which remain after the cycle i shrinks to a point in its basis. The notation D in formula (1) is usually adopted for the sum of all the basic determinants corresponding to the graph vertexes.

The kinetic analysis of a network of first order reversible reactions as sequence (I) was carried out by Wei and Prater.[3,4] Concerning sequence (I) one has to mention the calculation of only the numerators necessary for two r_s (r_2 and r_4) calculations[2] using formula (1). The main purpose of this note is to complete the calculations with all the necessary elements for the use of formula (1) to the sequence (I).

Calculations of r_s. The first stage as well as the second one are common to three cycles namely 123, 1245 and 12467. Correspondingly according to formula (1):

$$r_1 = \frac{1}{D}\{[\omega_1^+\omega_2^+\omega_3^+ - \omega_1^-\omega_2^-\omega_3^-](\omega_4^- + \omega_5^+)(\omega_6^- + \omega_7^+) + \omega_6^-\omega_7^+] +$$
$$[\omega_1^+\omega_2^+\omega_4^+\omega_5^+ - \omega_1^-\omega_2^-\omega_4^-\omega_5^-](\omega_6^- + \omega_7^+) + [\omega_1^+\omega_2^+\omega_4^+\omega_6^+\omega_7^+ - \omega_1^-\omega_2^-\omega_4^-\omega_6^-\omega_7^-]\}$$

$$r_2 = r_1$$

The third stage is common to cycles 123, 345 and 3467 and

$$r_3 = \frac{1}{D}\{[\omega_1^+\omega_2^+\omega_3^+ - \omega_1^-\omega_2^-\omega_3^-](\omega_4^- + \omega_5^+) + [\omega_3^-\omega_4^+\omega_5^+ - \omega_3^+\omega_4^-\omega_5^-](\omega_1^- + \omega_2^+)(\omega_6^- + \omega_7^+) +$$
$$[\omega_3^+\omega_4^+\omega_6^+\omega_7^+ - \omega_3^-\omega_4^-\omega_6^-\omega_7^-]\}$$

The fourth stage is common to cycles 345, 1245, 3467, 12467 and

$$r_4 = \frac{1}{D}\{[\omega_3^-\omega_4^+\omega_5^- - \omega_3^+\omega_4^-\omega^+](\omega_1^+ + \omega_2^+)(\omega_6^- + \omega_7^+) +$$
$$+ [\omega_1^+\omega_2^+\omega_4^+\omega_5^+ - \omega_1^-\omega_2^-\omega_4^-\omega_5^-](\omega_6^- + \omega_7^+) + [\omega\ \omega\ \omega\ \omega\ - \omega\ \omega\ \omega\ \omega\ ](\omega\ + \omega\ ) +$$
$$+ [\omega_3^-\omega_4^+\omega_6^+\omega_7^+ - \omega_3^+\omega_4^-\omega_6^-\omega_7^-](\omega_1^- + \omega_2^+) + [\omega_1^+\omega_2^+\omega_4^+\omega_6^+\omega_7^+ - \omega_1^-\omega_2^-\omega_4^-\omega_6^-\omega_7^-]\}$$

The fifth stage is common to cycles 567, 534, 1245 and

$$r_5 = \frac{1}{D}\{[\omega_5^+\omega_6^-\omega_7^- - \omega_5^-\omega_6^+\omega_7^+](\omega_3^+ + \omega_4^+)(\omega_1^- + \omega_2^+) + \omega_1^-\omega_2^+] +$$
$$+ [\omega_3^-\omega_4^+\omega_5^+ - \omega_3^+\omega_4^-\omega_5^-](\omega_1^- + \omega_2^+)(\omega_6^- + \omega_7^+) +$$
$$+ [\omega_1^+\omega_2^+\omega_4^+\omega_5^+ - \omega_1^-\omega_2^-\omega_4^-\omega_5^-](\omega_7^+ + \omega_8^-)\}$$

The sixth stage is common to cycles 567, 6734, 67124 and

$$r_6 = \frac{1}{D}\{[\omega_5^+\omega_6^-\omega_7^- - \omega_5^-\omega_6^+\omega_7^+](\omega_3^+ + \omega_4^-)(\omega_1^- + \omega_2^+) + \omega_1^-\omega_2^+ +$$
$$+ [\omega_3^-\omega_4^+\omega_6^+\omega_7^+ - \omega_3^+\omega_4^-\omega_6^-\omega_7^-](\omega_1^- + \omega_2^+) + [\omega_1^+\omega_2^+\omega_4^+\omega_6^+\omega_7^+ - \omega_1^-\omega_2^-\omega_4^-\omega_6^-\omega_7^-]\}$$

The seventh stage is common to cycles 567, 6734, 67124 thus

$$r_7 = r_6$$

In order to calculate the basic determinants of all the graph vertices we have to add the multiple edges directed toward the basis and to multiply the successive ones. By using such a procedure the following results were obtained:

$$
\begin{aligned}
D_{AZ} &= (\omega_4^+\omega_3^-)(\omega_6^-\omega_5^-)(\omega_7^+\omega_5^+)(\omega_1^+\omega_3^+) + (\omega_5^+\omega_7^-)(\omega_5^-\omega_6^-)(\omega_3^-\omega_4^-)(\omega_1^+\omega_2^-)\\
D_{BZ} &= (\omega_5^-\omega_6^+)(\omega_5^+\omega_7^-)(\omega_1^+\omega_3^-)(\omega_2^+\omega_3^-) + (\omega_1^-\omega_3^+)(\omega_1^-\omega_5^+)(\omega_5^-\omega_6^-)(\omega_3^-\omega_4^-)\\
D_{CZ} &= (\omega_5^+\omega_7^+)(\omega_1^+\omega_3^+)(\omega_2^+\omega_3^-)(\omega_3^-\omega_4^+) + (\omega_4^-\omega_6^-)(\omega_2^-\omega_3^-)(\omega_1^-\omega_3^+)(\omega_5^+\omega_7^-)\\
D_{DZ} &= (\omega_1^+\omega_3^+)(\omega_2^+\omega_3^+)(\omega_3^-\omega_4^+)(\omega_5^-\omega_6^+) + (\omega_4^-\omega_5^-)(\omega_3^-\omega_3^-)(\omega_2^-\omega^-)(\omega_1^-\omega_7^-)\\
D_Z &= (\omega_5^-\omega_6^-)(\omega_4^-\omega_6^-)(\omega_2^-\omega_3^-)(\omega_1^-\omega_2^-) + (\omega_2^+\omega_3^+)(\omega_3^-\omega_4^+)(\omega_1^+\omega_5^-)(\omega_6^-\omega_7^+)
\end{aligned}
\qquad \text{(II)}
$$

CONCLUSIONS

The graph theory permits the calculation of the reaction rate of a relatively complex system of reactions.

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