



# Multi-route reaction mechanism and steady-state flow: a MATLAB-based analysis

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## Abstract

This article presents the theoretical results for Multi-route reaction model of chemical kinetics. The steady-state approximation of the participating chemical species and the relationship between the common species in multi-routes mechanism is preserved. It has observed that some reaction routes complete their cycle before the others. The reason behind the reaction completion is the transition time of the species during the reaction. Graphical results obtained through MATLAB are used to describe the physical aspects of measurements.

**Keywords** Reaction mechanism · Steady state · Activation energy · Reaction routes

## Introduction

All chemical reactions that are classified into several categories i.e. simple and multiple reaction mechanisms, elementary and non-elementary reactions homogeneous and inhomogeneous reactions. Most chemical reactions are complex in nature, to cope with this type of reactions; the reaction mechanism consists of many chemical reaction phases called elementary phases (Constales et al. 2016; Shahzad and Sultan 2018; Shahzad et al. 2015a; Maxwell 1867). Many chemical systems that include homogeneous and heterogeneous reactions simultaneously with many applications, such as photosynthesis in plants, carbon dioxide and water converted to food due to photosynthesis. Batteries and combustion are the common examples of electrochemistry and polymer production (Sultan et al. 2019; Aris 1965).

By applying the Horiuti rule, the complex reaction mechanisms are divided into dissimilar available reaction paths (Shahzad et al. 2019a, 2020; Ali et al. 2019). While the smallest amount of energy is required to start the molecules or atoms in a situation where they can experience organic transformations. Before the reagents are converted

into products, the free energy of the system must exceed the activation energy for the reaction (Sultan et al. 2019; Yaublonsky et al. 2020). The classical reduction and modification methodologies for the dissimilar reaction pathways strongly depend on the approximations of the slow invariant manifold and the steady-state approximation (Shahzad et al. 2015b, 2016a, b, 2019b, c; Gorban and Shahzad 2011).

## Mathematical modeling

A flexible chemical reaction can be symbolized as:

$$\sum_{j=1}^n r_j R_j \Leftrightarrow \sum_{j=1}^n s_j S_j, \quad (1)$$

where  $r_j$  besides  $s_j$  are the stoichiometric coefficients of reactants and products and  $R_j, S_j$  are reactants and products. The reaction speed of each elementary step R can be measured by calculating its forward ( $R_f$ ) and backward ( $R_b$ ) reaction.

$$R = R_f^+ - R_b^- \quad (2)$$

The system (2) attains its equilibrium state when  $R_f^+ = R_b^-$ .

Applying mass action law, forward and backward reaction rates can be stated as:

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$$\begin{aligned} R_f^+ &= k^+ \prod c_{R_j}^{\gamma_j} = k^+ c_{R_1}^{\rho_1} c_{R_2}^{\rho_2} \\ R_b^- &= k^- \prod C_{S_j}^{\rho_j} = k^- c_{S_1}^{\rho_1} c_{S_2}^{\rho_2}. \end{aligned} \quad (3)$$

Here,  $C_{R_j}$ ,  $C_{S_j}$  are the concentration of reactant and product species,  $\gamma_j$ ,  $\rho_j$  are the stoichiometric coefficients and  $k^+$ ,  $k^-$  are the reaction rate coefficients for the forward and backward reactions, respectively.

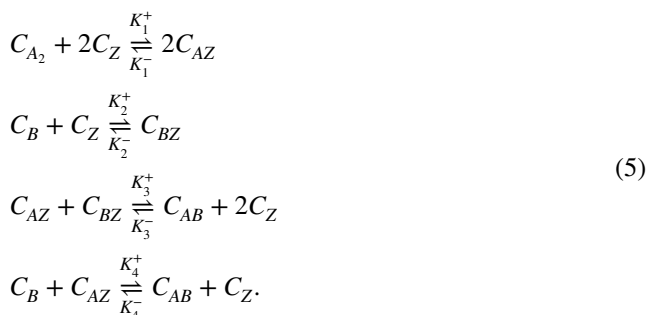
Finally, the addition of the product of rate equation and stoichiometric vectors gives equations of kinetics.

$$c_i' = \sum_{i=1}^n \alpha_i R_i(c). \quad (4)$$

## Mathematical model for reversible reaction mechanism

To study the different reaction paths, we necessity to consider a reversible non-homogeneous reaction mechanism in two ways that are of equal proportions with six chemical ingredients.

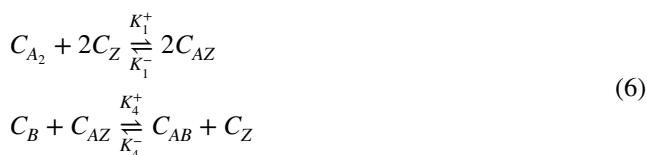
$C_{A_2}$ ,  $C_Z$ ,  $C_{AZ}$ ,  $C_{BZ}$ ,  $C_{AB}$  and  $C_B$ . Here, (A, Z and B) are three independent elements



The above reaction mechanism (5) can be divided in two different reaction routes by using Horiuti rule.

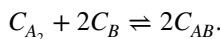
### First reaction route

An initial reaction-path completes its phase in the double steps 1st and 4th, total contributing chemical species in the first path are formed by three elements ( $N_e = 3$ ) are  $N_c = 5$ .



The Eq. (6) represents the double phase flexible reaction mechanism, now  $C_{A_2}$  and  $C_B$  responding to individually other in the existence of reagent Z provides the products  $C_{AB}$ .

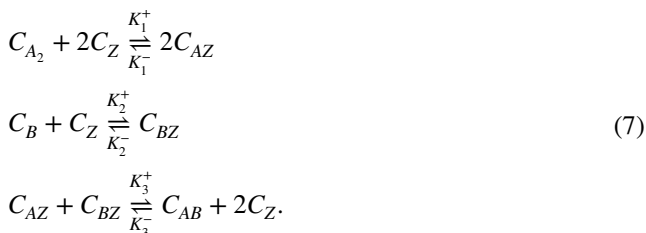
Increasing reaction comparison in 1st and 4th step with the Horiuti matrix  $[-1 - 2]^T$  individually we get.



The overall reaction mechanism involves three chemical species  $C_{A_2}$ ,  $2C_B$  and  $2C_{AB}$ , while  $2C_Z$ ,  $2C_{AZ}$  and  $2C_{AZ}$  are the surface intermediates.

### Second reaction route

The second reaction route completes their phase in 2nd, 3rd and 4th steps of their whole mechanism.



There are five chemical species ( $N_c = 5$ ) and three chemical elements ( $N_e = 3$ ) that are participating completely in their phase.

## Results and discussion

The goal of finding a state of equilibrium is generally to calculate the concentrations of the participating species and the elapsed time of the species in the two reaction paths. This period allows us to compare the efficiency of the two reaction pathways as a function of time.

Initially, the first reaction mechanism is considered with the initial parameters taken as,

$$c_1 = 0.5, c_2 = 0.1, c_3 = 0.1, c_4 = 0.4, c_5 = 0.1. \quad (8)$$

where  $C_1 = C_{A_2}$ ,  $C_2 = C_Z$ ,  $C_3 = C_{AZ}$ ,  $C_5 = C_{BZ}$ ,  $C_6 = C_{AB}$ ,  $C_4 = C_B$ .

The stoichiometric vectors of Eq. (2) are given by

$$\alpha_i = \begin{bmatrix} -1 & -2 & 2 & 0 & 0 \\ 0 & 1 & -1 & -1 & 1 \end{bmatrix}. \quad (9)$$

Equation (6) implies that



The reaction rates are given as  $R_1 = k_1^+ c_1 c_2^2 - K_1^- c_3^2$  and  $R_2 = k_2^+ c_3 c_4 - k_2^- c_2 c_6$ .

Now using Eq. (4) we develop the system equations of kinetic

$$\begin{aligned} c_1' &= -k_1^+ c_1 c_2^2 + K_1^- c_3^2 \\ c_2' &= 2k_1^- c_3^2 + k_2^+ c_3 c_4 - 2k_1^+ c_1 c_2^2 - k_2^- c_2 c_6 \\ c_3' &= 2k_1^+ c_1 c_2^2 - 2k_1^- c_3^2 - k_2^+ c_3 c_4 + k_2^- c_2 c_6 \\ c_4' &= k_2^+ c_2 c_5 - k_2^- c_3 c_4 \\ c_5' &= k_2^+ c_3 c_4 - k_2^- c_2 c_6. \end{aligned} \tag{11}$$

The reduced description form the system (11) in  $c_1$  and  $c_4$  is

$$\begin{aligned} c_1' &= -k_1^+ c_1 (2c_1 - c_4 - 0.5)^2 + k_1^- (-2c_1 + c_4 + 0.7)^2, \\ c_4' &= -k_2^+ (2c_1 - c_4 - 0.5)(0.5 - c_4) + k_2^- c_4 (-2c_1 + c_4 + 0.7). \end{aligned}$$

Likewise, the initial parameters for the second path of the reaction mechanism are:

$$c_1 = 0.500000000, c_2 = 0.1, c_3 = 0.1, c_4 = 0.4, c_5 = 0.2, c_6 = 0.1.$$

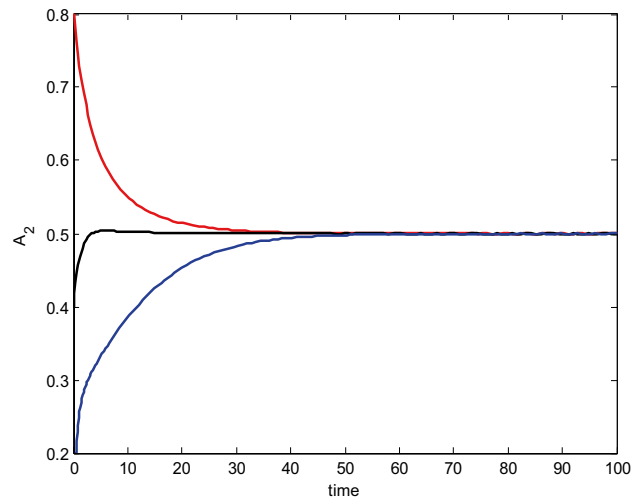
Vectors are stoichiometric

$$\alpha_i = \begin{bmatrix} -1 & -2 & 2 & 0 & 0 & 0 \\ 0 & -1 & 0 & -1 & 0 & 1 \\ 0 & 2 & -1 & 0 & 1 & -1 \end{bmatrix}. \tag{12}$$

Now we denote the species with different constant,  $c_1 = C_{A_2}, c_2 = C_Z, c_3 = C_{AZ}, c_4 = C_B, c_5 = C_{BZ}, c_6 = C_{AB}$ .  
Now Eq. (7) implies that

$$\begin{aligned} C_1 + 2C_2 &\overset{K_1^+}{\underset{K_1^-}{\rightleftharpoons}} 2C_3 \\ C_4 + C_2 &\overset{K_2^+}{\underset{K_2^-}{\rightleftharpoons}} c_6 \\ C_3 + C_6 &\overset{K_3^+}{\underset{K_3^-}{\rightleftharpoons}} C_5 + 2C_2. \end{aligned} \tag{13}$$

$$\begin{aligned} c_1' &= -k_1^+ c_1 c_2^2 + k_1^- c_3^2 \\ c_2' &= -2k_1^+ c_1 c_2^2 + 2k_1^- c_3^2 - k_2^+ c_2 (2c_1 + 2c_3 + c_2 - 0.9) + k_2^- (0.3 - c_2 - c_3) + 2k_3^+ c_3 (0.3 - c_2 - c_3) \\ &\quad - 2k_3^- (1.3 - 2c_1 - c_3)c_2^2 + 2k_3^+ c_3 \times (0.6 - c_2 - c_3) - 2k_3^- c_2^2 (1.35 - 2c_1 - c_3) \\ c_3' &= 2k_1^+ c_1 c_2^2 - 2k_1^- c_3^2 - k_3^+ c_3 (0.3 - c_2 - c_3) + k_3^- (1.3 - 2c_1 - c_3)c_2^2. \end{aligned} \tag{16}$$



**Fig. 1** The transition time period of  $A_2$   $k_1^+ = 1; k_1^- = 0.5; k_2^+ = 0.5; k_2^- = 1$  with started initial points 0.2, 0.4 and 0.8 approaches to its balanced state of three possible kinds of trajectories

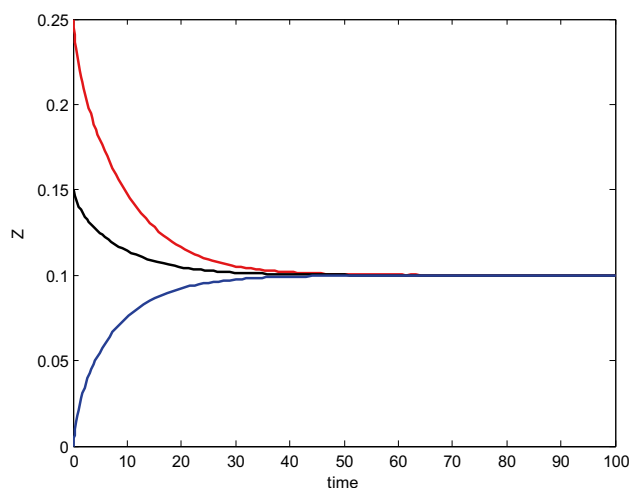
Here

$$\begin{aligned} R_1 &= R_{f1}^+ - R_{b1}^- = k_1^+ c_1 c_2^2 - k_1^- c_3^2, R_2 = R_{f2}^+ - R_{b2}^- = k_2^+ c_2 c_4 - k_2^- \\ &\text{and } R_3 = R_{f3}^+ - R_{b3}^- = k_3^+ c_3 c_6 - k_3^- c_5 c_2^2. \end{aligned} \tag{14}$$

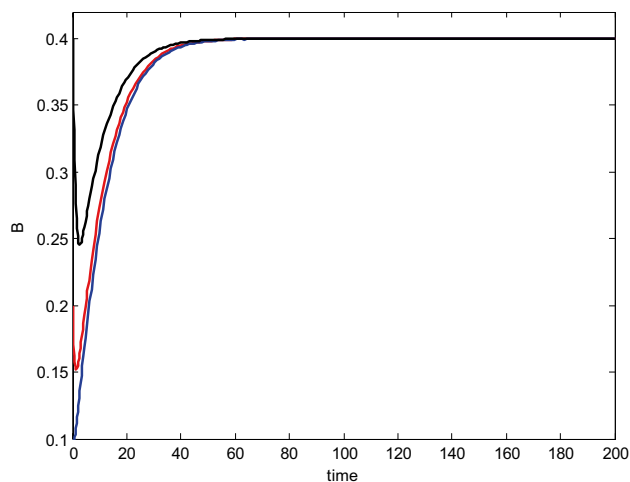
The system of equations for the second reaction route can be defined as:

$$\begin{aligned} c_1' &= -k_1^+ c_1 c_2^2 + k_1^- c_3^2 \\ c_2' &= -2k_1^+ c_1 c_2^2 + 2k_1^- c_3^2 - k_2^+ c_2 c_4 + k_2^- c_6 + 2k_3^- c_3 c_6 - 2k_3^+ c_5 c_2^2 \\ c_3' &= 2k_1^+ c_1 c_2^2 - 2k_1^- c_3^2 - k_3^+ c_3 c_6 + k_3^- c_5 c_2^2 \\ c_4' &= -k_2^+ c_2 c_4 + k_2^- c_6 \\ c_5' &= k_3^+ c_3 c_6 - k_3^- c_5 c_2^2 \\ c_6' &= -k_3^+ c_3 c_6 + k_3^- c_5 c_2^2 + k_2^+ c_2 c_4 - k_2^- c_6. \end{aligned} \tag{15}$$

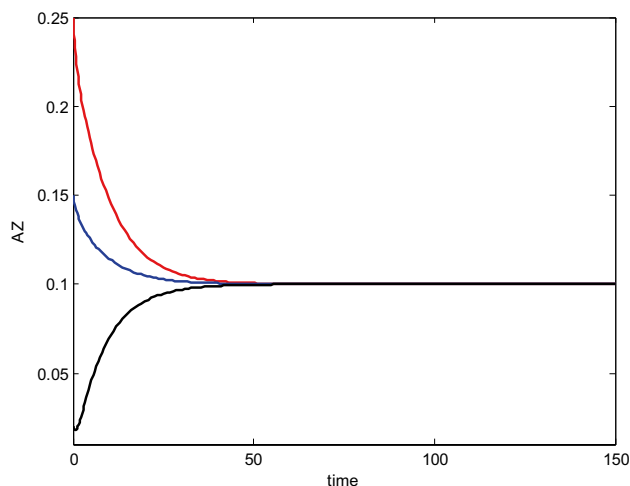
The reduced form of the system of differential Eq. (15) is



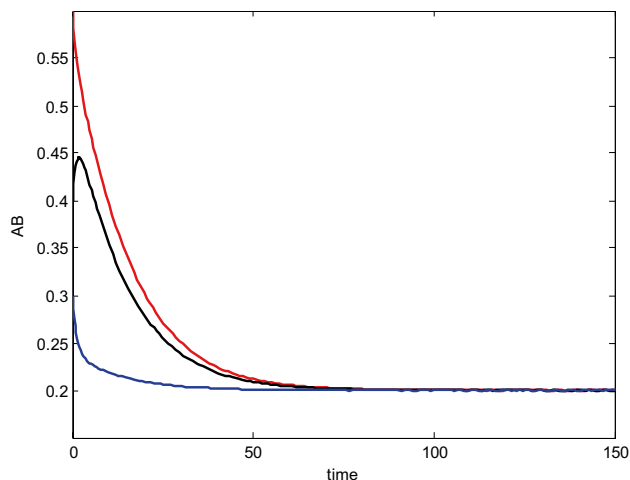
**Fig. 2** The transition time period of Z  $k_1^+ = 1$ ;  $k_1^- = 0.5$ ;  $k_2^+ = 0.5$ ;  $k_2^- = 1$  with started initial points 0, 0.15 and 0.25 approaches to its balanced state of three possible kinds of trajectories



**Fig. 4** The transition time period of B  $k_1^+ = 1$ ;  $k_1^- = 0.5$ ;  $k_2^+ = 0.5$ ;  $k_2^- = 1$  with started initial points 0.1, 0.2 and 0.3 approaches to its balanced state of three possible kinds of trajectories



**Fig. 3** The transition time period of AZ  $k_1^+ = 1$ ;  $k_1^- = 0.5$ ;  $k_2^+ = 0.5$ ;  $k_2^- = 1$  with started initial points 0.02, 0.15 and 0.25 approaches to its balance state of three possible kind of trajectories

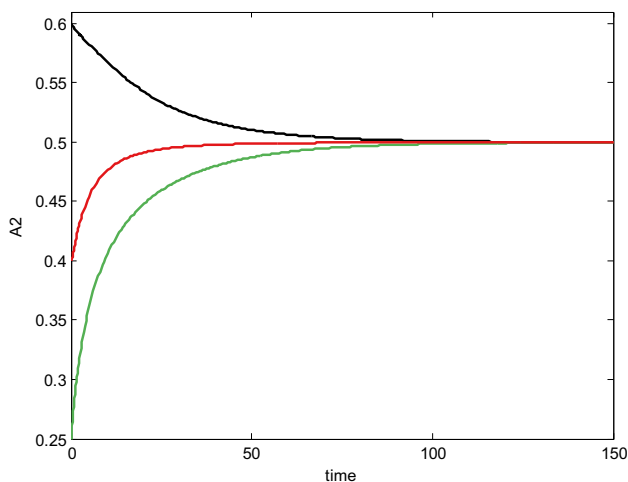


**Fig. 5** The transition time period of AB  $k_1^+ = 1$ ;  $k_1^- = 0.5$ ;  $k_2^+ = 0.5$ ;  $k_2^- = 1$  with started initial points 0.3, 0.4 and 0.6 approaches to its balanced state of three possible kinds of trajectories

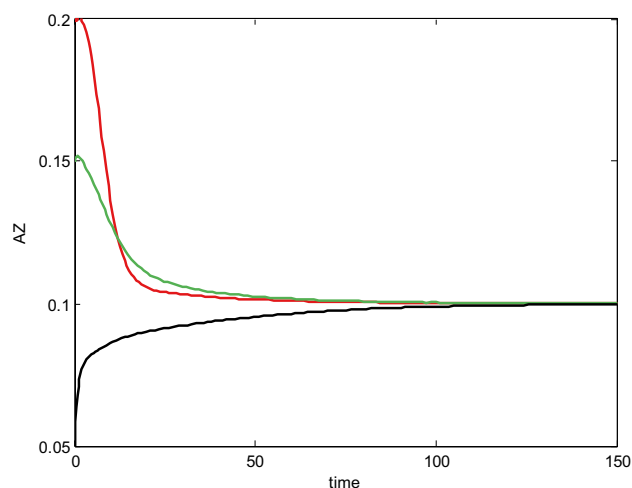
Here,  $k_1^+ = 1$  and  $k_2^+ = 0.5 = k_3^+$ .

Based on Figs. 1, 2, 3, 4, and 5, we can observe the transition time used by each chemical species A<sub>2</sub>, Z, AZ, B and AB at constant speeds and the first route from different initials and all trajectories takes a steady-state condition after completing their transition time. While, the transition time used by each chemical species A<sub>2</sub>, Z, AZ, B, AB and BZ for second reaction route can be observed at constant speeds in Figs. 6, 7, 8, 9, 10, and 11.

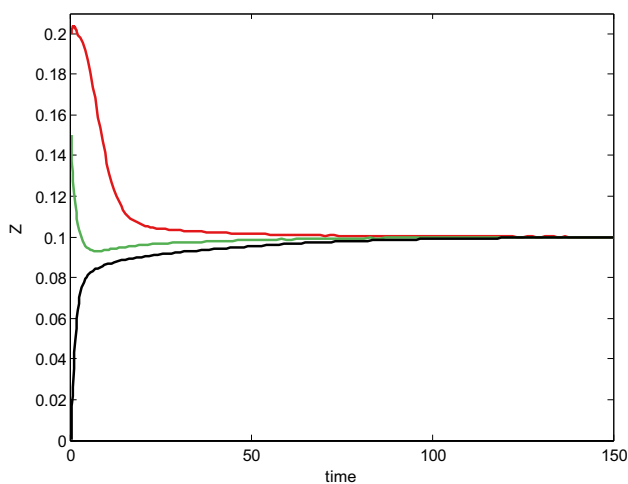
Species participating in these two paths approach their equilibrium after passing through a different transition period but have a different period of time. This shows that some reactions are faster than others (Figs. 12, 13, 14, 15, and 16).



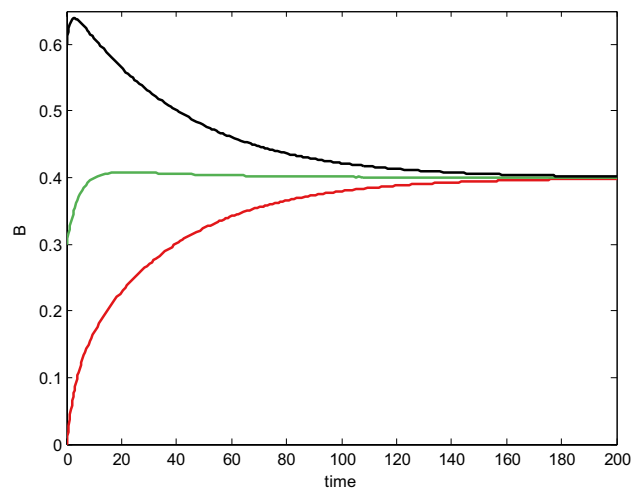
**Fig. 6** The transition time period of  $A_2$   $k_1^+ = 1$ ;  $k_1^- = 0.5$ ;  $k_2^+ = 0.5$ ;  $k_2^- = 0.2$ ;  $k_3^+ = 0.5$ ;  $k_3^- = 2.5$  with started initial points 0.25, 0.4 and 0.6 approaches to its balanced state of three possible kinds of trajectories



**Fig. 8** The transition time period of  $Z$   $k_1^+ = 1$ ;  $k_1^- = 0.5$ ;  $k_2^+ = 0.5$ ;  $k_2^- = 0.2$ ;  $k_3^+ = 0.5$ ;  $k_3^- = 2.5$  with started initial points 0.06, 0.15 and 0.2 approaches to its balanced state of three possible kinds of trajectories



**Fig. 7** The transition time period of  $Z$   $k_1^+ = 1$ ;  $k_1^- = 0.5$ ;  $k_2^+ = 0.5$ ;  $k_2^- = 0.2$ ;  $k_3^+ = 0.5$ ;  $k_3^- = 2.5$  with started initial points 0.15, 0 and 0.2 approaches to its balanced state of three possible kinds of trajectories

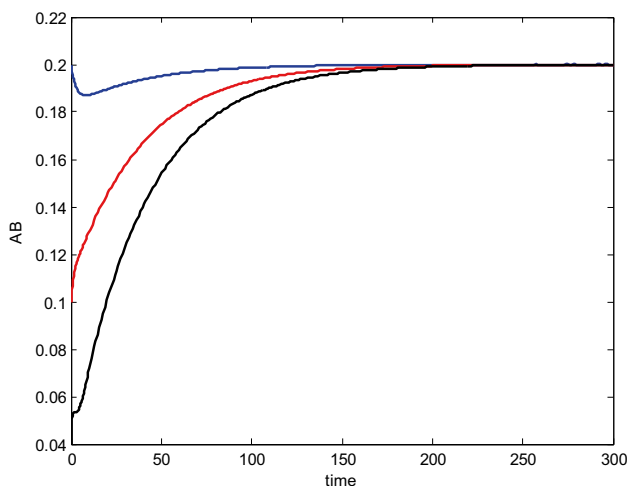


**Fig. 9** The transition time period of  $B$   $k_1^+ = 1$ ;  $k_1^- = 0.5$ ;  $k_2^+ = 0.5$ ;  $k_2^- = 0.2$ ;  $k_3^+ = 0.5$ ;  $k_3^- = 2.5$  with started initial points 0.3, 0 and 0.6 approaches to its balanced state of three possible kinds of trajectories

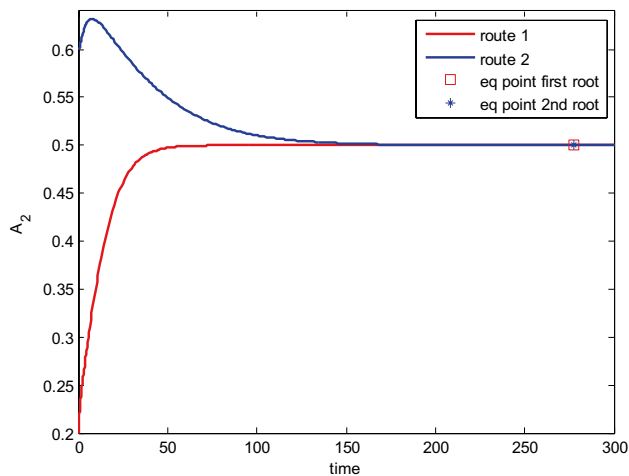
### Conclusion

Analysis of steady-state approximation in both reaction routes is a step towards the understanding the slow and fast behavior of complex chemical reactions. The present dogma states that the behavior of chemical species in both

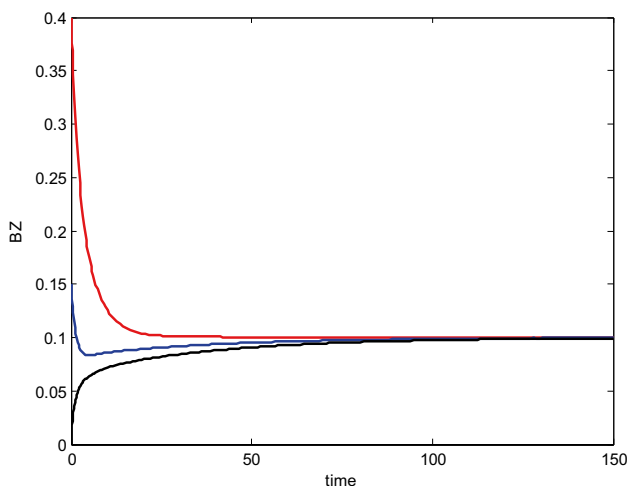
routes approaching towards their equilibrium after passing through a different transition period but they have a different time period. This shows that some reactions are faster than the others. Similarly, it indicates that the activation energy requires for the system is different in both the reaction routes.



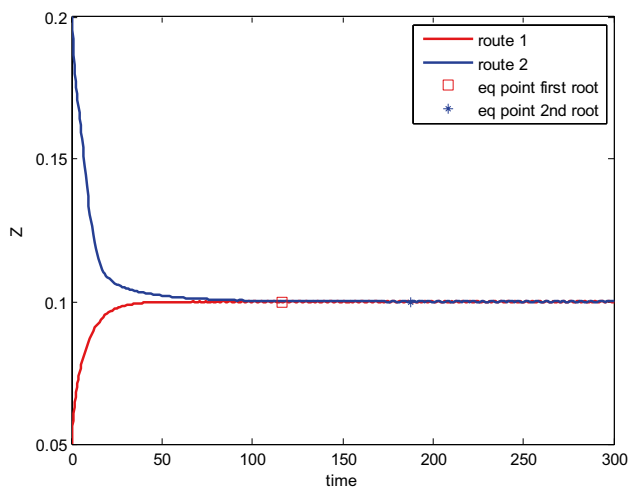
**Fig. 10** The transition time period of AB  $k_1^+ = 1$ ;  $k_1^- = 0.5$ ;  $k_2^+ = 0.5$ ;  $k_2^- = 0.2$ ;  $k_3^+ = 0.5$ ;  $k_3^- = 2.5$  with started initial points 0.04, 0.1 and 0.2 approaches to its equilibrium state of three possible kinds of trajectories



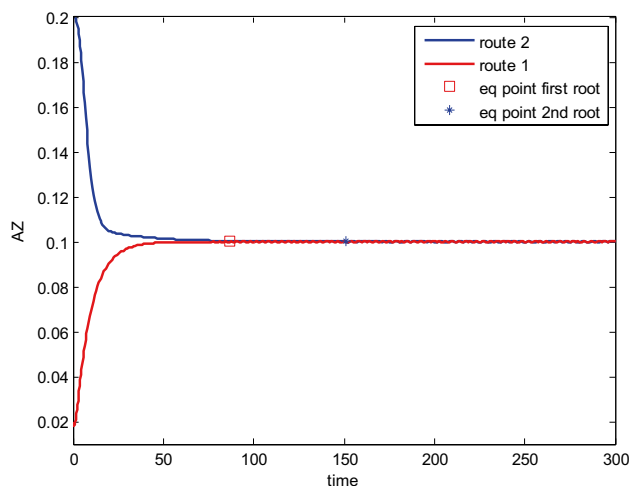
**Fig. 12** The comparison between two species ( $A_2$  and  $A_2$ ) for both reaction routes are given as the first and second routes attain their equilibrium position at a point 277.8, respectively



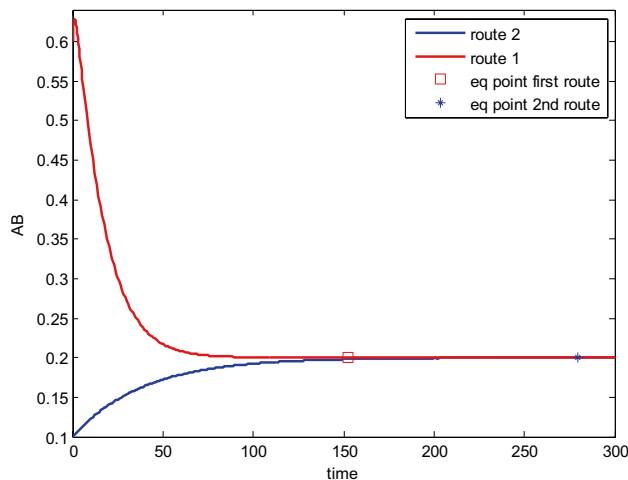
**Fig. 11** The transition time period of B  $k_1^+ = 1$ ;  $k_1^- = 0.5$ ;  $k_2^+ = 0.5$ ;  $k_2^- = 0.2$ ;  $k_3^+ = 0.5$ ;  $k_3^- = 2.5$  with started initial points 0.15, 0 and 0.4 approaches to its balanced state of three possible kinds of trajectories



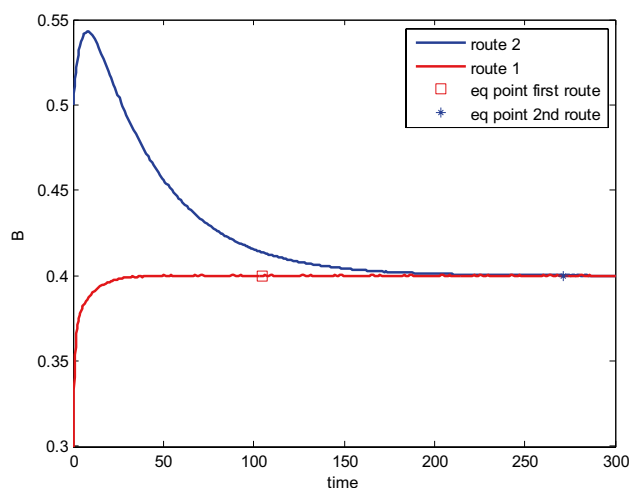
**Fig. 13** The comparison between two species ( $Z$  and  $Z$ ) for both reaction routes are given as, the first path attain their equilibrium position at a point 116.7 and the second path attain their equilibrium position at a point 187.4, respectively



**Fig. 14** The comparison between two species ( $AZ$  and  $AZ$ ) for both reaction paths are given as the first path attain their equilibrium position at a point 86.9 and the second path attain their equilibrium position at a point 150.7, respectively



**Fig. 16** The comparison between two species ( $AB$  and  $AB$ ) for both reaction paths are given as the first path attain their equilibrium position at a point 152.7 and the second path attain their equilibrium position at a point 279.5, respectively



**Fig. 15** The comparison between two species ( $B$  and  $B$ ) for both reaction paths are given as the first path attain their equilibrium position at a point 104.5 and the second path attain their equilibrium position at a point 271.6, respectively

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