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ORIGINAL ARTICLE

Evaluation of steady-state to identify the fast-slow completion-route in the multi-route reaction mechanism

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Abstract
The multi-route reversible chemical scheme involves several chemical species and needs to inspect their behavior, activation energy, and the transition period before attaining equilibrium. The comparison between the transition periods of each reaction route is perceived. However, the behavior of the involved species in a multi-routes of the reaction mechanism is presented graphically. The computational procedure is adopted by using MATLAB.

Keywords Reaction mechanism · Transition period · Reaction routes · Reaction route comparison

Introduction

Form the last 3 decades, the collaboration between mathematics and chemistry were bloom. The most dominating name of pioneers in constructing the concept of stoichiometry is Lavoisier and Dalton, on the parallel bases, Cayley is the maker of matrices theory. In the 1950–1960s, the renew computational results on the interface of mathematics and chemistry had made. In the current era, in mathematical chemistry, many severe hypotheticals are easily to fathom. There is a vast application of chemical reactions like the process of burning, rust, the formation of many useful chemicals and systems of biochemical regularly that's why we cannot neglect the enthusiastic role of chemistry in our domestic or industrials level (Kooshkbaghi et al. 2014; Shahzad et al. 2015a; Aris 1965; Constales et al. 2016; Maxwell 1867; Boltzmann 1970). Many researchers develop their interest in the field of complex chemical reaction mechanisms and serve their efforts. By the brief knowledge of chemical mechanisms, we can get access to the complication of chemistry. Many microscopic species take part in chemical reactions (Sultan et al. 2019b, 2020; Shahzad et al. 2015b, 2016a, 2019a; Kooshkbaghi et al. 2016;). It is difficult to handle these species easily. For this, we need to model the microscopic system mathematically and then find their features (Shahzad et al. 2019b,2019c,2016b; Gorban and Karlin 2003).

The analysis of this article demonstrates the steady-state behavior of reduced species in the reaction mechanism and the transition time for the common species of both reaction routes. Although both routes are not in the same dimension, we have delivered the new idea of their unique equilibrium lies in the respective domain. Moreover, it is observed from the above discussion that the current consideration is unique, and no such analysis has been reflected before in the literature.

Chemical reactions

Firstly, we need to construct the model of the complex chemical reaction mechanism that may occur through a series of distinct steps, known as stoichiometric mechanisms. Each of these steps can be written as a chemical equation, i.e., if we have ith chemical species A_i, participating in chemical reactions then sth generic stoichiometric mechanisms can be written as:

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$$\sum_{s=1}^{n} \alpha_{si} \cdot A_i \rightarrow \sum_{s=1}^{n} \beta_{si} \cdot A_i. \tag{1}$$

These formal sums $\sum_{i=1}^{n} \beta_{si} \cdot A_i = (\beta_s, A)$ appearing on both sides of each elementary reactions are called complexes Θ_i. Thus the above system (1) can be rewritten as $\Theta_i^- \rightarrow \Theta_i^+$. The set of complexes for the given reaction mechanism will become $\Theta_i, ..., \Theta_q$, while they may be different from each other or coincide in some cases, therefore, $q < 2n$.

Reaction routes

Further, the complexity of the mechanism can be reduced to study the multi-route reaction mechanism separately. Here we follow the mathematical model for multiple reaction routes mechanism (Sultan et al. 2019a) (Fig. 1).

In two-route graphs with a common step, there are three domains, but only two domains are separate, and so there are two independent reaction routes given in Fig. 2.

To deliberate the different kinetics patterns in detail, a four-step reaction mechanism is considered (Constales et al. 2016; Sultan et al. 2019a). The reaction mechanism with common step adopts two reaction routes and seven chemical components $C_4H_{10}, Z, C_4H_8Z, H_2, C_4H_8, C_4H_6Z$ and C_4H_6 formed by three chemical elements (C, H and Z).

$$\begin{aligned}
&C_4H_{10} + Z \overset{k_1^{\pm}}{\rightleftharpoons} C_4H_8Z + H_2\\
&C_4H_8Z \overset{k_2^{\pm}}{\rightleftharpoons} C_4H_8 + Z\\
&C_4H_8Z \overset{k_3^{\pm}}{\rightleftharpoons} C_4H_6Z + H_2\\
&C_4H_6Z \overset{k_4^{\pm}}{\rightleftharpoons} C_4H_6 + Z.
\end{aligned} \tag{2}$$

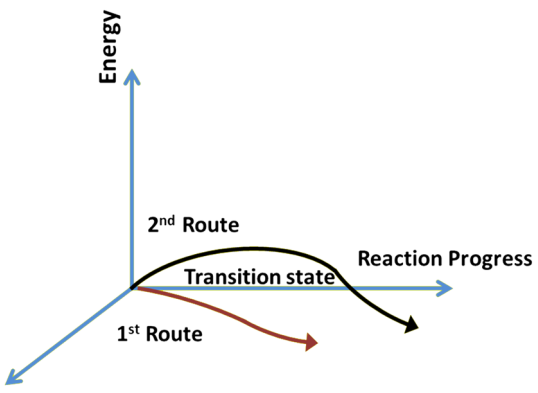

Fig. 1 General representation of multi-route reaction mechanism, first route (lies in R^2) and the second route (lies in R^3) in its reduced form

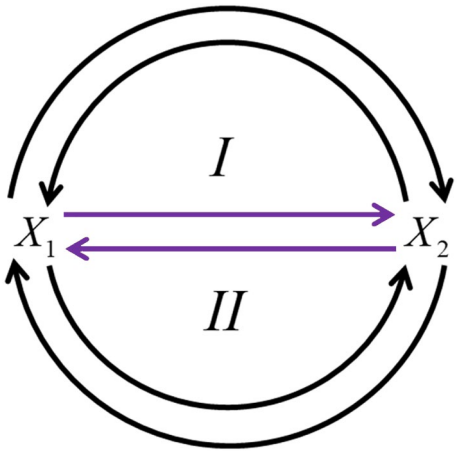

Fig. 2 A two-route reaction mechanism with a common step

Now, we need to calculate the steady-state approximation of all chemical species for both reaction routes and compare their transition time-period of the system (2). Firstly, examine the first-route of the reaction mechanism which gives the product in the first and second steps. The initial constraints are chosen as:

$$\begin{aligned}
&C_4H_{10} = c_1 = 0.5,\ Z = c_2 = 0.2,\ C_4H_8Z = c_3 = 0.1\,, H_2 = c_4 = 0.4,\\
&C_4H_8 = c_5 = 0.2,\ C_4H_6 = c_6 = 0.1,\ C_4H_6Z = c_7 = 0.1\\
&\text{with } k_1^+ = 1,\ k_2^+ = 1,\ k_3^+ = 0.1.
\end{aligned} \tag{3}$$

Finally, the kinetic equations are the sum of the product of their stoichiometric vectors and rate equations (Shahzad and Sultan 2018).

$$\dot{c} = \sum_{s=1}^{r} \gamma R_s(c). \tag{4}$$

First route

A complex chemical reaction involves

$$\begin{aligned}
&C_4H_{10} + Z \rightleftharpoons C_4H_8Z + H_2\\
&C_4H_8Z \rightleftharpoons C_4H_8 + Z.
\end{aligned} \tag{5}$$

The above chemical mechanisms can be written as

$$\begin{aligned}
&c_1 + c_2 \rightleftharpoons c_3 + c_4\\
&c_3 \rightleftharpoons c_5 + c_2.
\end{aligned} \tag{6}$$

Reaction rates are given by the mass action law, i.e.,

$$\begin{aligned}
R_1 &= R_{f1}^+ - R_{b1}^- = k_1^+ c_1 c_2 - k_1^- c_3 c_4\\
R_2 &= R_{f2}^+ - R_{b2}^- = k_2^+ c_3 - k_2^- c_5 c_4.
\end{aligned} \tag{7}$$

and their stoichiometric vectors are

$$r_1 = [-1, -1, 1, 1, 0]$$
$$r_2 = [0, 1, -1, 0, 1] \tag{8}$$

$$\mathrm{Dc} = \mathrm{const}\begin{bmatrix} 4 & 0 & 4 & 0 & 4 \\ 10 & 0 & 8 & 2 & 8 \\ 0 & 1 & 1 & 0 & 0 \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \end{bmatrix} = \begin{bmatrix} \mathrm{const}_1 \\ \mathrm{const}_2 \\ \mathrm{const}_3 \end{bmatrix}. \tag{9}$$

The kinetic equations for our system (4) are given by:

$$\begin{aligned} \dot{c}_1 &= k_1^- c_3 c_4 - k_1^+ c_1 c_2 \\ \dot{c}_2 &= k_1^- c_3 c_4 - k_1^+ c_4 c_2 - k_2^- c_4 c_5 - k_2^+ c_3 \\ \dot{c}_3 &= k_1^+ c_1 c_2 - k_1^- c_3 c_4 - k_2^+ c_3 + k_2^- c_4 c_5 \\ \dot{c}_4 &= k_1^+ c_1 c_2 - k_1^- c_3 c_4 \\ \dot{c}_5 &= k_2^+ c_3 - k_2^- c_4 c_5. \end{aligned} \tag{10}$$

Second route

The second route of the reaction mechanism is given as:

$$\begin{aligned} &\mathrm{C_4H_{10}} + \mathrm{Z} \rightleftharpoons \mathrm{C_4H_8Z} + \mathrm{H_2} \\ &\mathrm{C_4H_8Z} \rightleftharpoons \mathrm{C_4H_6Z} + \mathrm{H_2} \\ &\mathrm{C_4H_6Z} \rightleftharpoons \mathrm{C_4H_6} + \mathrm{Z}. \end{aligned} \tag{11}$$

The above chemical mechanisms can be written as

$$\begin{aligned} &c_1 + c_2 \rightleftharpoons c_3 + c_4 \\ &c_3 \rightleftharpoons c_5 + c_2 \\ &c_5 \rightleftharpoons c_6 + c_2. \end{aligned} \tag{12}$$

The kinetic equations for the second route of reaction mechanism are:

$$\begin{aligned} \dot{c}_1 &= k_1^- c_3 c_4 - k_1^+ c_1 c_2 \\ \dot{c}_2 &= k_3^+ - k_1^+ c_4 c_2 - k_1^- c_4 c_6 - k_1^- c_3 c_4 \\ \dot{c}_3 &= k_1^+ c_1 c_2 - k_1^- c_3 c_4 - k_2^+ c_3 + k_2^- c_4 c_5 \\ \dot{c}_4 &= k_2^+ c_3 + k_1^+ c_1 c_2 - k_2^- c_4 c_5 - k_1^- c_3 c_4 \\ \dot{c}_5 &= k_2^+ c_3 - k_2^- c_4 c_5 + k_3^- c_2 c_6 - k_3^+ c_5 \\ \dot{c}_6 &= k_3^+ c_5 - k_3^- c_2 c_6. \end{aligned} \tag{13}$$

Graphical results

The steady-state behaviors of chemically reacting species of both routes are given in Figs. 3a–e and 4a–e, respectively at their equilibrium points. The initial trajectories that are starting from different initial points and approaching towards the equilibrium point after completing their transition time-period.

The behavior and transition time of involving species in the second route is discussed in Fig. 4a–e.

A mathematical methodology has implemented to observe the transition period of each chemical species involved in both reaction routes. It is perceived from Figs. 3a–e and 4a–e that the transition time taken by each chemical species $\mathrm{C_4H_{10}}$,$\mathrm{C_4H_8}$, Z,$\mathrm{C_4H_8}$, Z, $\mathrm{C_4H_6}$, $\mathrm{C_4H_6Z}$ and $\mathrm{H_2}$ of both first and second route is different.

Reaction route comparison w.r.t time

Here we have addressed the comparison of common species of two different routes. It is clear from Fig. 5a–e, the first reaction rout completes its transition time-period faster than the second route.

Concluding remarks

In this article, we have measured the transition period of the same species involved in the two-route complex reaction mechanism. The behavior of the involved species is presented graphically with the following outcomes.

- Different time-period of common species have been observed through different initials.
- The involved species in both routes approach towards their equilibrium after passing through a different transition period.
- This indicates the different behavior of the same species in different routes.

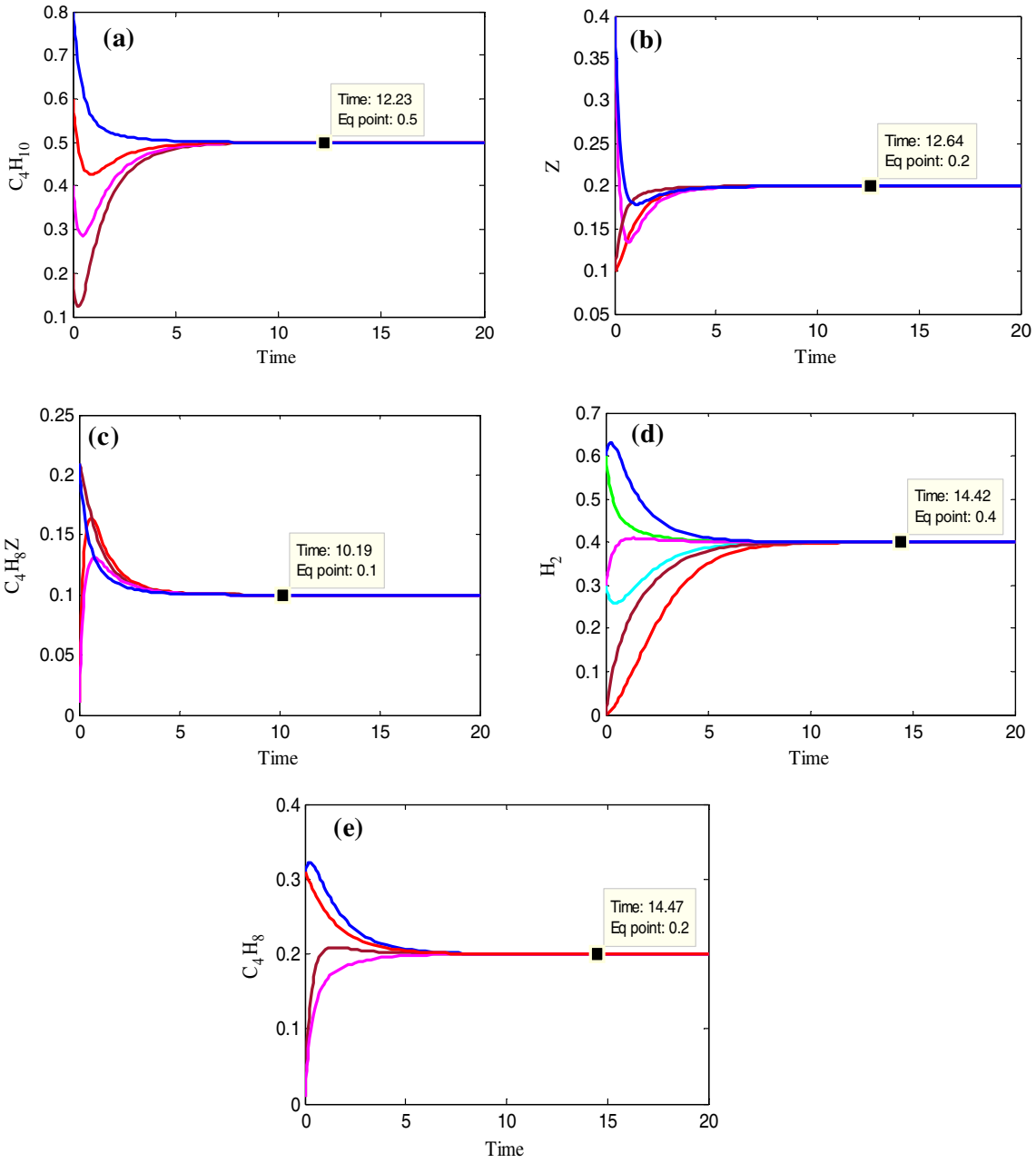

Fig. 3 **a–e** Trajectories of first reaction-route after completing their transition time with different initials moving towards their equilibrium points

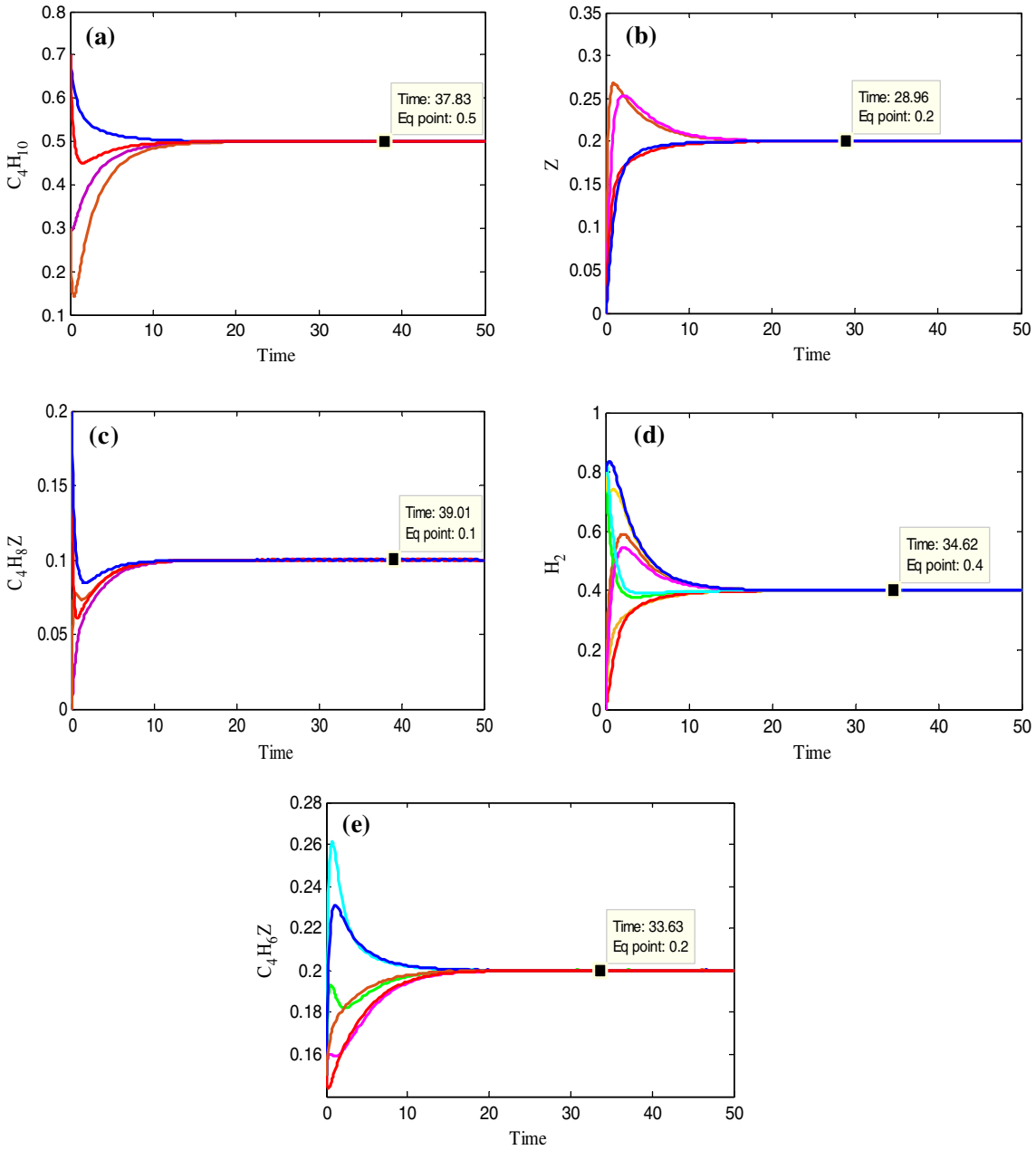

Fig. 4 **a**–**e** Trajectories for second reaction-route after completing their transition time with different initials moving towards their equilibrium points

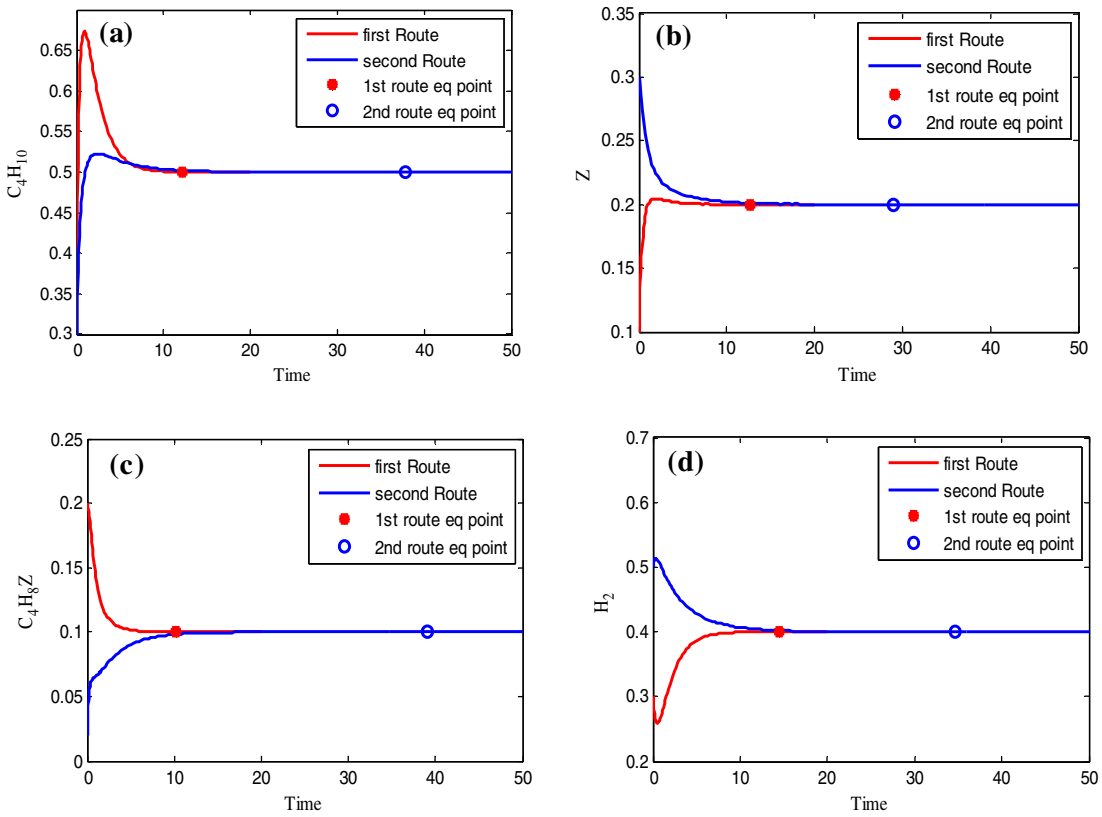

Fig. 5 **a–d** Comparison of common species of both reaction-routes w.r.t time

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