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Research Note

Computational analysis of the slow invariant manifold for single and multi-route reaction mechanisms

M. Shahzad[a,*], **M. Ali**[a], **F. Sultan**[a,*], **and W. Azeem Khan**[b,c]

a. *Department of Mathematics and Statistics, Hazara University, Mansehra 21300, Pakistan.*
b. *School of Mathematics and Statistics, Beijing Institute of Technology, Beijing 100081, China.*
c. *Department of Mathematics, Mohi-ud-Din Islamic University, Nerian Sharif, 12010 Azad Jammu & Kashmir, Pakistan*

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Abstract. Many natural phenomena such as ecosystems, earth climate, animals, living cells, and human brain are characterized each by their own complex behavior. Therefore, a new field called "systems chemistry" has emerged that aims to capture the complexity of natural systems within a synthetic chemical framework. To understand the physical behavior of chemical components in a reaction mechanism (system), the overall (complete) reaction network and different available reaction paths should be perceived on a deeper level. To this end, the present study develops a multi-route reaction mechanism for a complex chemical reaction problem, which is unsolvable through common ways. Further, invariant manifold approximation is constructed through quasi equilibrium manifold. Numerical results are shown in the graphical form in MATLAB.

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1. Introduction

Chemical reactions play a vital role in our daily life and ecosystem. Industries playing a major role in the development of human society are dependent on chemical reactions, i.e., chemical industries utilizing many emerging applications in fine chemical and pharmaceuticals. Analysis of these reactions is essential to achieving any related objectives. Reaction mechanisms vary from simple to complex depending on their corresponding nature and structure. Therefore, both experimental and theoretical investigations represent necessary parts of the mechanism. Different methods and numerical techniques have been proposed so far to deal with complexities of a reaction mechanism [1–6]. There exists a non-trivial interaction between mathematics and mathematical modeling of complex systems [7,8]. In order to develop advanced and proficient numerical methods, such approximate models that are submissive to numerical analysis should be formulated. Further to this, computer-oriented methods facilitate qualitative and quantitative analyses of mathematical models.

The objective of the present research is to bring together different available modern mathematical methods and models that are commonly used to rethink and change complex chemical problems, biological problems, ideas, and methods and to establish new applicable ideas within a defined domain so as to ensure greater understanding and achieve progress.

According to Maxwell [9], all intermediate complexes are in immediate equilibrium with free substrates and enzymes, which represent a purely Quasi Equilibrium (QE) assumption. Boltzmann [10] offered the same idea for the Boltzmann kinetics.

In the modeling of a chemical problem, a kinetic mathematical model may not respect thermodynamic

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[*] *Corresponding authors.*
E-mail addresses: shahzadmaths@hu.edu.pk (M. Shahzad); faisal_maths@hu.edu.pk (F. Sultan)

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conditions at first. In this case, a system can be solved by deforming the entropy (linearly) with the provided agreement between the kinetic model and deformed thermodynamics [11].

Through mathematical modeling, one can transform a higher dimensional, non-linear and multi-route complex chemical reaction into a low-dimension single-route reaction mechanism [12–14]. Based on the construction of a reduced dissipative system, the method of the invariant manifold is applied [15–17] and the invariant grids for a system are constructed. The idea was first presented in [18] and involves the following steps:

- Approximate the initial curves for both reaction routes through Quasi Equilibrium Manifold (QEM), Spectral Quasi Equilibrium Manifold (SQEM), or Intrinsic Low Dimension Manifold (ILDM);
- Refine it by the method of invariant grids;
- Compare the trajectories of the solutions of both routes graphically rather than in the tabulated form;
- Measure the overall reaction, if possible.

2. Research methodology

In order to study chemical reactions, it should be considered that kinetic measurements are followed by mass action law; then, in the reversible reaction mechanism, the presence of equilibrium c^{eq} (detailed, i.e., atomic) indicates the stability function (Lyapunov) in the form of free entropy:

$$G = \sum_{i=1}^{n} c_i[\ell n(c_i/c_i^{eq}) - 1] \rightarrow \min . \tag{1}$$

By starting from the initial point (equilibrium) and proceeding to the next grid point $c_{n+1} = c_n + \delta c_n$, with the addition of shift vector δc_n, the corresponding grid point on QEM is defined using the system in the form of reduced description ξ (let's say). To evaluate the solution behavior of slow chemical species, the slowest left-side eigenvector c_s^l that corresponds to the minimum absolute eigenvalue of the Jacobian matrix J measured at each grid point (through Schur decomposition method) must be selected. Then, a particular solution trajectory is constructed.

From Figure 1, it is clear that, there are three different directions available at each grid point to proceed to. According to ILDM, we will proceed further with slow space $n_S = n - n_F$. This will allow us to distinguish between the fast subspace and slow space on the basis of the eigenspace measured at each point in the phase space of the system:

$$\max \{reV_{c_i},\ i = 1 \cdots n_F\} < K$$
$$< \min \{reV_{c_i},\ i = n_{F+1} \cdots n\}, \tag{2}$$

and to stop further movement on the fast subspace.

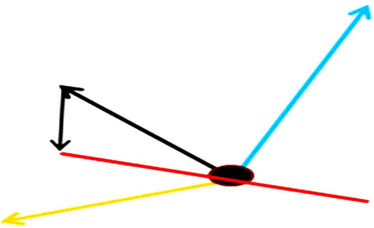

Figure 1. Projected vector field over the tangent space.

This reduction technique is basically based on the decoupling of fast-equilibrium chemical progressions from slower dynamics and promotes the motion on the dimensional slow invariant manifold.

Solution trajectories can be measured using any unmeasured system of n_F equations for n-variables. Then, the concentration space is split into a direct sum of the fast C_F (intermediate species) subspace and the slow C_S (terminal species) subspace, i.e., $C = C_F \oplus C_S$.

While the fast subspace C_F is fast with fixed values of C_S, the fast subsystem relaxes into a stationary state like $C : C_F \rightarrow C_F^{qss}(C_S)$ and slow variables remain unchanged. This assumption will become a purely quasi-steady-state approximation, and it can be written in the mathematical form as follows:

$$J = J_S + J_F, \tag{3}$$

i.e.:

$$\dot{C}_F = J_F(C_F \oplus C_S), \tag{4}$$

when:

$$C_S = const \qquad \text{and} \qquad C_F \rightarrow C_F^{qss}(C_S), \tag{5}$$

$$\dot{C}_S = J_S(C_S \oplus C_F^{qss}(C_S)). \tag{6}$$

In simple words, the initial layer of the system, usually called initial trajectory, will be measured at first. Then, the slow system will be solved. It is also possible that additional balances of slow variables arise when a fast subsystem goes into equilibrium.

2.1. Mathematical model

To derive sensitive equations, a mathematical model (using SQEM technique [2,6]) is constructed for the single-route reaction mechanism; then, the multi-route reaction mechanism is formulated.

2.1.1. A four-step single-route reaction mechanism

Herein, a four-step reaction mechanism is considered below:

$$C_A \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} C_B, \qquad C_B \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} C_C,$$

$$C_C \underset{k_3^-}{\overset{k_3^+}{\rightleftharpoons}} C_A, \qquad C_A + C_B \underset{k_4^-}{\overset{k_4^+}{\rightleftharpoons}} 2C_C, \tag{7}$$

with the initial parameters given below:

	α_1	α_2
$C_4H_{10}+Z \rightleftharpoons C_4H_8Z+H_2$	1	1
$C_4H_8Z \rightleftharpoons C_4H_8+Z$	1	0
$C_4H_8Z \rightleftharpoons C_4H_6Z+H_2$	0	1
$C_4H_6Z \rightleftharpoons C_4H_6Z+Z$	0	1

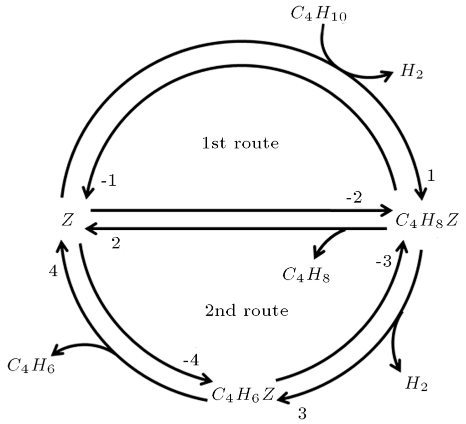

Figure 2. Two-route butane mechanism.

$$C_A^*=c_1^*=0.1, \quad C_B^*=c_2^*=0.5, \quad C_C^*=c_3^*=0.4. \tag{8}$$

Assume that the Lyapunov function G takes the following form:

$$G=\sum_{i=1}^{3} c_i\left[\ln\left(\frac{c_i}{c_i^*}\right)-1\right]. \tag{9}$$

The kinetic equations of the three-component vector of the concentration $c=[c_1,c_2,c_3]$ will take the following form:

$$\dot{c}=\sum_{i=1}^{4} r_i R_i, \tag{10}$$

where r_i's are the stoichiometric vectors:

$$r_1=\begin{pmatrix}-1 & 1 & 0\end{pmatrix}, \qquad r_2=\begin{pmatrix}0 & -1 & 1\end{pmatrix},$$

$$r_3=\begin{pmatrix}1 & 0 & -1\end{pmatrix}, \qquad r_4=\begin{pmatrix}-1 & -1 & 2\end{pmatrix}. \tag{11}$$

Moreover, R_i represents reaction rates:

$$R_1=k_1^+c_1-k_1^-c_2, \qquad R_2=k_2^+c_2-k_2^-c_3,$$

$$R_3=k_3^+c_3-k_3^-c_2, \qquad R_4=k_4^+c_1c_2-k_4^-c_3^2. \tag{12}$$

The Jacobian matrix at the equilibrium point is as follows:

$$J(c^*)=\begin{bmatrix}-8.0\times10^1 & -7.5\times10^0 & 3.6\times10^1\\ -3.0\times10^1 & -2.2\times10^1 & 4.0\times10^1\\ 1.1\times10^2 & 3.0\times10^1 & -7.6\times10^1\end{bmatrix}. \tag{13}$$

The slowest left-side eigenvector V_l^s obtained by the minimum absolute eigenvalue is:

$$V_l^s=\begin{bmatrix}-0.8552 & 0.4303 & -0.2889\end{bmatrix}. \tag{14}$$

The gradient and the second derivative matrix H (Enthalpy) of Lyapunov function G are:

$$\nabla G=\begin{bmatrix}\ln c_1-\ln c_1^*\\ \ln c_2-\ln c_2^*\\ \ln c_3-\ln c_3^*\end{bmatrix}, \qquad H=\begin{bmatrix}1/c_1 & 0 & 0\\ 0 & 1/c_2 & 0\\ 0 & 0 & 1/c_3\end{bmatrix}. \tag{15}$$

2.1.2. *A four-step multi-route reaction mechanism*

A four-step mechanism is considered in which methane reacts with the surface catalysis to form an intermediate species. At the next step, the intermediate species is converted into a product. This process requires two different routes to complete the dehydrogenation process. A four-step mechanism is considered with seven chemical components, C_4H_{10}, Z, C_4H_8Z, H_2, C_4H_8, C_4H_6Z, C_4H_6Z and C_4H_6, and three independent elements (C, H and Z (*a surface catalyst*)).

As shown in Figure 2, there are two reaction routes, i.e., $N_{rr}=4-3+1=2$. The first and second routes lie in the 2D and 3D phase spaces, respectively.

Figure 3 comparatively presents the idea of the first route (lies in R^2) and the second route (lies in R^3).

Now, the invariant manifold should be measured for both reaction routes and their results are to be compared in a phase space. First, the first route of the reaction mechanism is examined, which gives the product in the first and second steps. For the sake of convenience, the initial parameters are chosen as follows:

$$C_4H_{10}=c_1=0.5, \qquad Z=c_2=0.2,$$

$$C_4H_8Z=c_3=0.1, \qquad H_2=c_4=0.4,$$

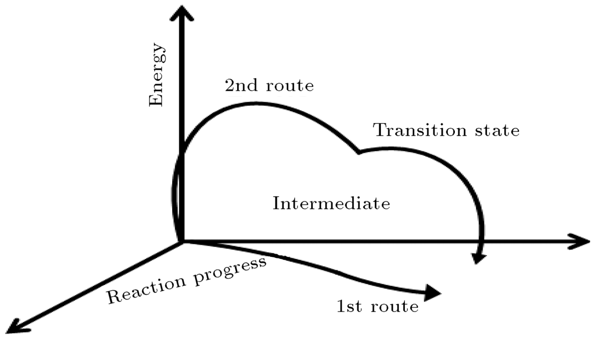

Figure 3. General representation of double-route reaction mechanism.

$$C_4H_8 = c_5 = 0.2, \qquad C_4H_6 = c_6 = 0.1, \tag{16}$$

$$\frac{d\left[C_4H_{10}\right]}{dt} = k_1^- \left[C_4H_8Z\right]\left[H_2\right] - k_1^+ \left[C_4H_{10}\right]\left[H_2\right],$$

$$\frac{d[Z]}{dt} = k_2^+ \left[C_4H_8Z\right] - k_1^+ \left[C_4H_{10}\right]\left[H_2\right]$$

$$+ k_1^- \left[C_4H_8Z\right]\left[H_2\right] - k_2^- \left[C_4H_8\right]\left[H_2\right],$$

$$\frac{d\left[C_4H_8Z\right]}{dt} = k_1^+ \left[C_4H_{10}\right]\left[H_2\right] - k_2^+ \left[C_40H_8Z\right]$$

$$-k_1^- \left[C_4H_8Z\right]\left[H_2\right] + k_2^- \left[C_4H_8\right]\left[H_2\right],$$

$$\frac{d\left[H_2\right]}{dt} = k_1^+ \left[C_4H_{10}\right]\left[H_2\right] - k_1^- \left[C_4H_8Z\right]\left[H_2\right],$$

$$\frac{d\left[C_4H_8\right]}{dt} = k_2^+ \left[C_4H_8Z\right] - k_2^- \left[C_4H_8\right]\left[H_2\right], \tag{17}$$

where $k_1^+ = 1$, $k_2^+ = 2$, and $k_3^+ = 1$, $k_4^+ = 0.5$ (for the second route).

The first slowest eigenvector, which is delivered from the Jacobean matrix of System (17), is evaluated at the equilibrium point as follows:

$$v^{sl} = \begin{bmatrix}0.3407 & 0.0141 & -0.0282 & -0.42558 & -0.8376\end{bmatrix}. \tag{18}$$

3. Model reduction method and analysis of results

In the case where SQEM is taken as an initial approximation, an n-dimensional slowest left-side eigenvector, which provides information about the reduced descripted variable υ, is required. System (17) takes the following form:

$$\sum_{i=1}^{n} \langle t_j, \rho_i \rangle \upsilon_i = -\left(t_j, \nabla G(c)\right), \qquad \forall\, j = 1,$$

$$\sum_{i=1}^{n} \upsilon_i^2 = \varepsilon, \qquad \varepsilon = 0.005, \tag{19}$$

where ρ_i is the basis of a molecular matrix. The matrix E will take the following form:

$$E = \begin{bmatrix}\nu_i^s \\ M\end{bmatrix}, \tag{20}$$

with the vector t spanning $ker(E)$.

Thus, by starting from the equilibrium points and proceeding to the next nodal point (left and right) with shift vector $c_{n+1} = c_n + \delta c_n$, the following initial curves can be obtained for single-route and multi-route reaction mechanisms.

The objective here is to observe the behavior of the reduced chemical species in single- and multi-route reaction mechanisms. In this regard, a brief description of the single-route four-step reaction mechanism is given.

3.1. Single-route reaction mechanism

For the right and left nodal points, $c_{\tilde{B}n+1} > c_{\tilde{B}n}$ (Figure 4) and $c_{\tilde{B}n+1} < c_{\tilde{B}n}$ (Figure 5) are considered, respectively, while Figure 6 combines both of the left and right branches.

The solution behavior of reduced species close to the equilibrium point is shown in Figure 7, while SQEM initial approximation with their solution trajectories is shown in Figure 8.

3.2. Multi-route mechanism

The behavior of reduced species in the first and second routes is highlighted in Figures 9 and 10. The solution trajectories of both reaction routes (in R^2, R^3 spaces) are reported in Figures 11 and 12, respectively. The

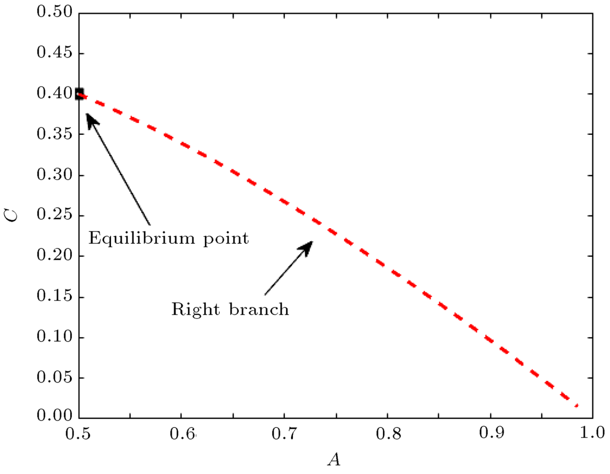

Figure 4. Right branch of the initial approximation starting from equilibrium point.

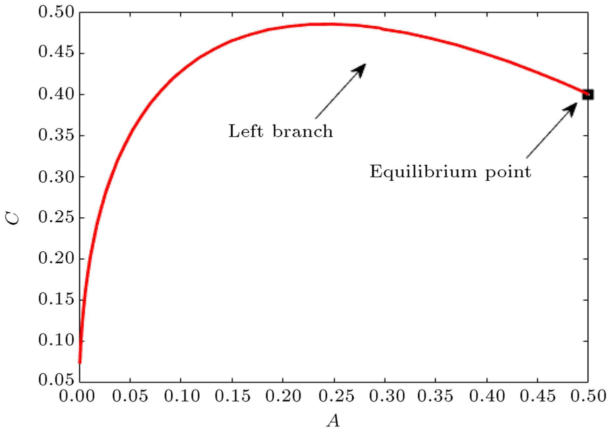

Figure 5. Initial approximation in the backward direction (left branch) from the equilibrium point.

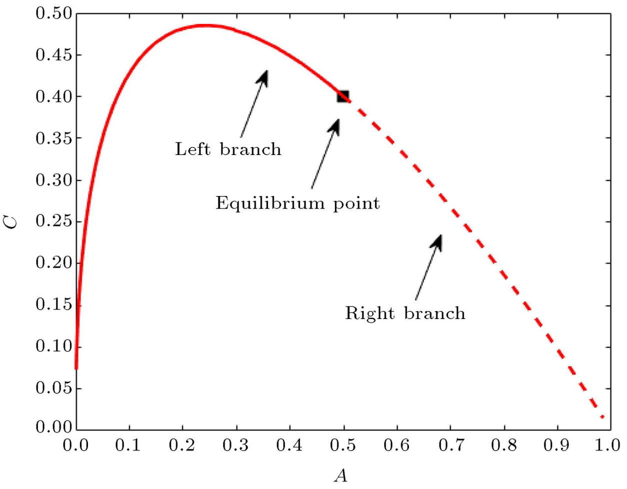

Figure 6. Initial approximation (both left and right directions).

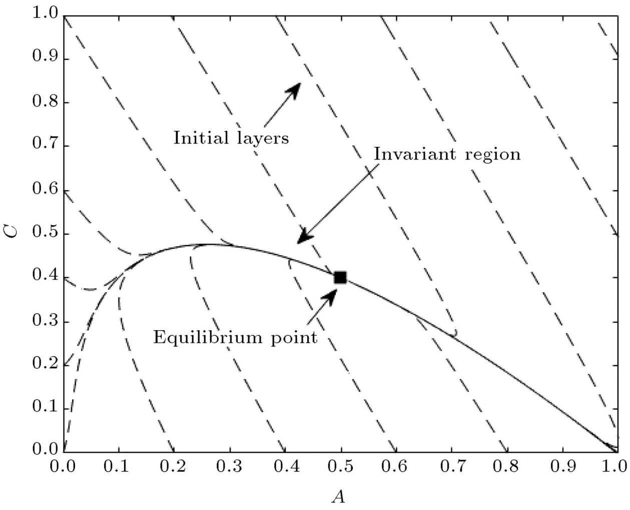

Figure 7. The individual trajectories in phase plane $[A\ C]$ for four-step reaction mechanism.

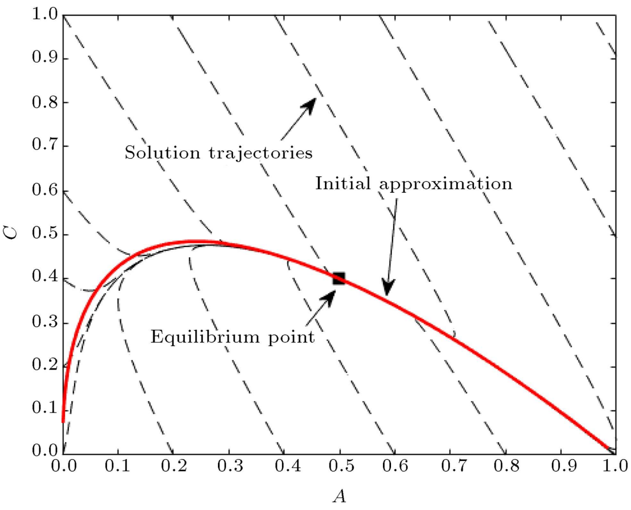

Figure 8. Initial approximation of four-step mechanism and solution trajectories.

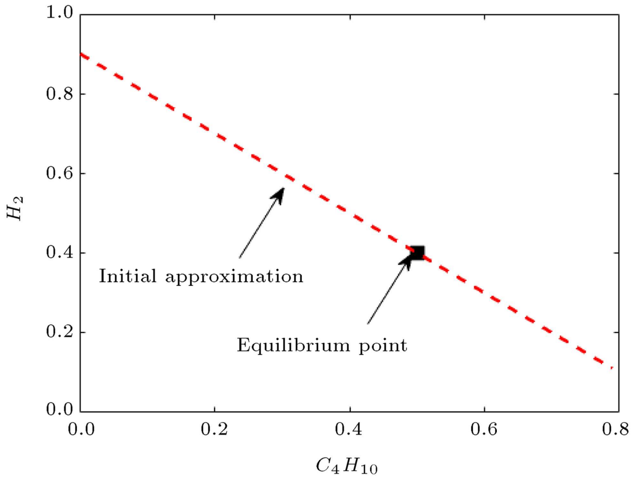

Figure 9. Initial approximation of the first reaction route (Route-1).

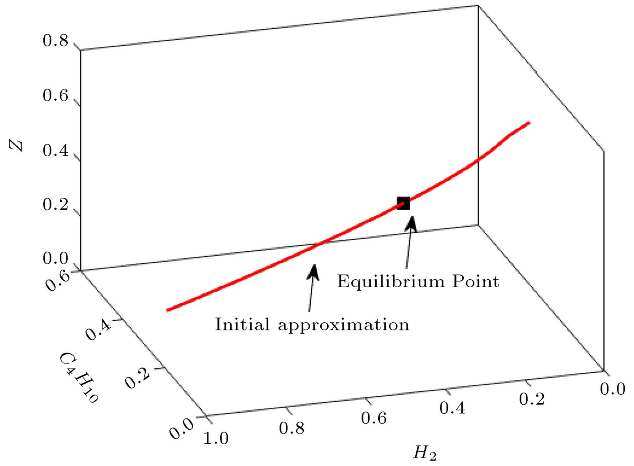

Figure 10. Initial approximation of the second reaction route obtained by Spectral Quasi Equilibrium Manifold (SQEM) technique (Route-2).

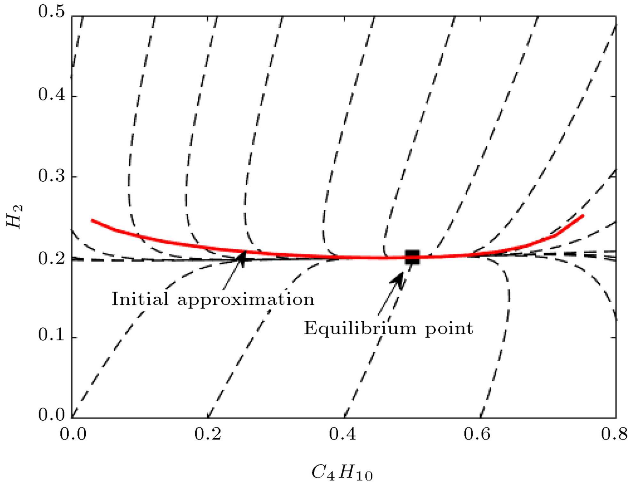

Figure 11. Solution trajectories on phase plane $[C_4H_{10}, H_2]$ for the first route of multi-route mechanism, and initial approximation along with solution trajectories.

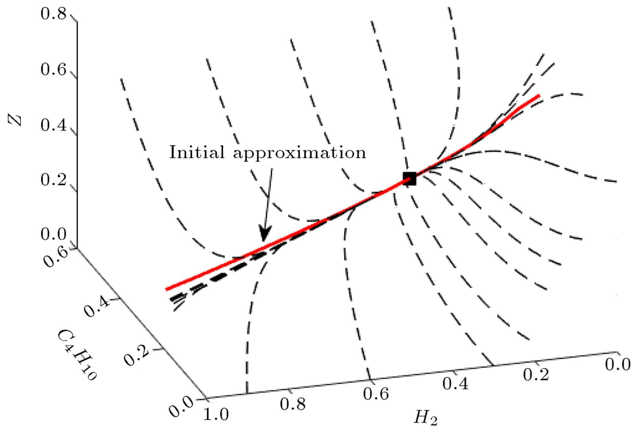

Figure 12. Solution trajectories and initial approximation in the 3D space [C_4H_{10}, H_2, Z] for the second route of multi-route mechanism.

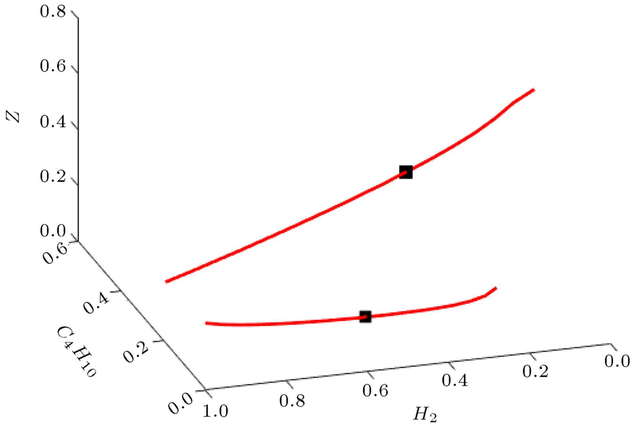

Figure 13. Comparison of reaction routes in terms of initial approximations.

process is completed as soon as complex nodes are obtained.

3.3. Reaction route comparison with respect to Slow Invariant Manifold (SIM)

At this stage, the initial approximation (SIM) obtained through both of reaction routes is compared. While the first route was on a plane, the second route was in space. As shown in Figure 13, the solution curves (R^2, R^3) were obtained at the equilibrium points and were compared in terms of their solution trajectories, as evident in Figure 14.

The numerical values of the reduced species of both reaction routes are described in Table 1.

4. Conclusion

The following outcomes were achieved in this study:

- Adoption of different available completion routes (cyclic paths, Figure 2) in any complex chemical reactions allows removing the stiffness of a complex chemical problem. Otherwise, due to different transition periods, stiffness may remain in the prevailing equations of the system;
- Comparison of different available methods allows distinguishing the best one;
- Graphical representation of the results clears the idea of Slow Invariant Manifold (SIM).

Table 1. Initially approximated node points of the 1st and 2nd routes of reaction mechanism.

Reaction routes	First reaction route		Second reaction route		
Serial no.	C_4H_{10}	H_2	C_4H_{10}	H_2	Z
1	0.3375	0.5625	0.3883	0.1621	0.1871
2	0.3777	0.5223	0.4159	0.2210	0.1886
3	0.4183	0.1817	0.4438	0.2806	0.1916
4	0.4590	0.4410	0.4717	0.3403	0.1948
5	0.5	0.4	0.5	0.4	0.2
6	0.5410	0.3590	0.5283	0.4597	0.2052
7	0.5825	0.3175	0.5570	0.5192	0.2130
8	0.6244	0.2756	0.5860	0.5787	0.2230
9	0.6671	0.2329	0.6158	0.6379	0.2376
10	0.7104	0.1896	0.0946	0.0916	0.0940

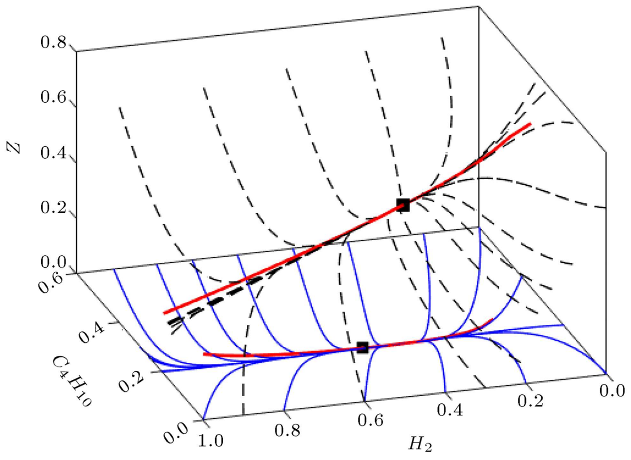

Figure 14. Comparison of reaction routes in terms of slow invariant manifold and behavior of chemical species close to their equilibrium point.

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Biographies

Muhammad Shahzad is working at the Department of Mathematics & Statistics, Hazara University, Mansehra, Pakistan. He has completed his PhD at the University of Leicester, UK. His research interests lie in modern model reduction by numerical/computational techniques. He has published more than 50 papers in well-reputed journals and delivered different scientific lectures in national and international conferences and workshops. As a HOD, he remained involved in different statutory bodies for more than five years.

Mehboob Ali is a PhD student at the Department of Mathematics & Statistics, Hazara University, Mansehra, Pakistan. His research interests lie in computational fluid dynamics. He has published more than 49 papers in well-reputed journals.

Faisal Sultan is a PhD student at the Department of Mathematics & Statistics, Hazara University, Mansehra, Pakistan. His research interests lie in modern model reduction by numerical/computational techniques. He has published more than 40 papers in well-reputed journals.

Waqar Azeem Khan is working at the School of Mathematics and Statistics, Beijing Institute of Technology, Beijing 100081, China. He has completed his PhD at the Quaid-I-Azam University, Islamabad, Pakistan. His research interests lie in computational fluid dynamics. He has published more than 50 papers in well-reputed journals and delivered different scientific lectures in national and international conferences and workshops.