Journal of Mathematical Chemistry
https://doi.org/10.1007/s10910-023-01565-6

ORIGINAL PAPER

Slow invariant manifold assessment for efficient production of H_2SO_4 by SO_2: a computational approach

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Received: 24 July 2023 / Accepted: 29 November 2023

Abstract

Sulfur dioxide (SO_2) belongs to the highly reactive group of gases familiar as "Oxides of Sulfur". SO_2 has lots of adverse effects on plants, respiratory system and many other environmental issues. Sulfur dioxide is a primary pollutant which is regulated worldwide, due to the combustion of fuel. Different approaches are adopted to economically control the SO_2 in the environment which causes the production of sulfuric acid that is reflected in acid rain. The aim of this study is to investigate the invariant regions and solution pathways for the formation of H_2SO_4 in a multi-step reaction mechanism. The employed Model Reduction Techniques (MRTs) such as Spectral Quasi Equilibrium Manifold (SQEM) and Intrinsic Low Dimensional Manifold (ILDM) give the solution curves, which functions as a primary approximation to invariant manifold. It is achieved that each chemical specie can be assessed rather than taking the overall mechanism. The new discovery suggests that we could achieve the invariant regions for SO_2 and H_2SO_4. SO_2 emissions, along with emission norms, will be disclosed. The comparison of MRTs is depicted through tabular and graphical representations, while theoretical results are demonstrated through computer simulations using MATLAB.

Keywords Mathematical modelling · Model reduction techniques · Slow invariant manifolds · Chemical kinetics

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Published online: 10 January 2024

1 Introduction

The Clean Air Act of 1970 mentions six air pollutants: Sulfur dioxide, carbon monoxide, ozone, nitrogen dioxide, and lead. The high emission of SO_2 is responsible for environmental and human health problems and acidification of water and soil. Some health issues due to SO_2 are arising like breathing difficulties, respiratory illness and cardiovascular diseases, etc. Due to solvability in water, it can be oxidized with airborne water droplets to produce Sulfuric acid (H_2SO_4). As well, chemical reactions are significant for the ecosystem and our daily life [1]. For this purpose, the analysis of complex reactions is a difficult task in reaction kinetics [2].

Chemical kinetics' "problem of reduced description" refers to the difficulty of synthesizing intricate chemical reaction networks into a smaller number of reactions and species that sufficiently represent the fundamental actions of the system. The study of chemical kinetics includes the factors that affect chemical reaction rates and the rates at which chemical reaction occur [3]. In the many real-world contexts, including combustion, atmosphere, the networks of chemical reactions in biology and chemistry can be exceedingly expansive and complex having a wide variety of reactions and involved species. Simulating the intricate system, nevertheless, can be time and money consuming in terms of computing.

Reduced description methods seek to address these issues by creating simplified models that nevertheless contain the key characteristics of the system. Typically, these simplified models entail grouping together complexity, a method for reducing description is the Quasi Steady-State Approximation [4, 5]. This strategy presumes that some species reach a steady state, and their concentrations fluctuate more slowly than those of other species during the reaction process.

The method of partial equilibrium is an alternative strategy that works under the premise that certain reactions reach equilibrium significantly more quickly than others if these processes equilibrate quickly [6]. The involved species concentrations can be calculated separately. Validating and improving these simplified models by for experimental findings to be reliable and applicable, comparisons with more in depth simulations are essential.

The problem of reduced description in chemical kinetics is generally a considerable, but it was successfully decreased by developing models, researchers may learn about intricate systems and develop the more manageable simulations for use in practical applications. Complexity is extended with the extended number of steps or several species (ions, atoms, molecules). Many methods and techniques have been developed to minimize the complexity of complex reactions [7]. The complexity of reaction mechanism can be reduced without effecting the originality of mechanism by applying different MRTs while considering the reaction's fast and slow phases [8, 9]. A necessary work of MRTs is to investigate the approximate solution curves in phase space, solution trajectories for reduced species approaches to their equilibrium point by completing their transitional periods with different initials [10–12]. From a mathematical point of view, such a type of invariant region is called slow invariant manifold in lower dimension [13].

Two most essential methods to analysis the complex reactions with higher dimensions are ILDM and SQEM [14, 15]. The decomposed structure simplifies the model so that the desired properties of the solution can be achieved without affecting the complete reaction mechanism. Macroscopic and microscopic analysis of complex chemical systems is deduced from chemical kinetics and physically used variables during the time scales [16]. Different types of reaction mechanisms change their behavior concerning their composition and nature. So, their theoretical and experimental inquisitions have a vital role in comprehending chemical mechanisms. It is essential to explore how the emission of gases from industry and other vehicles creates ecological problems in the form of acid rain.

The main objective of this study is the comparison of solution behavior and Slow Invariant Manifold (SIMs) among the chemical species to decode the complexity for the formulation of sulfuric acid in the multi-step chemical reaction. Also, the comparison of invariant solutions obtained through different MRTs to investigate the best available technique.

2 Theoretical background

2.1 Kinetic pattern constructions and MRTs

For the mechanisms of complex chemical reaction with m elementary reaction steps in any closed system, the reaction rate γ can be found and investigated using forward γ^+ and backward rates γ^- of reactions of elementary steps, respectively.

$$\sum_{i=1}^{k} \alpha_{ji} A_i \Leftrightarrow \sum_{i=1}^{k} \beta_{ji} A_i, \quad j = 1, ...m \tag{1}$$

where

$$\gamma = \gamma^+ - \gamma^- \tag{2}$$

Here A_i is represents the chemical components and α_{ji} &β_{ji} are reaction coefficients, k_s^+ and k_s^- are the forward and backward rate constants, respectively. Now, for the jth step stoichiometric vector is given for every $v_{ji} = \beta_{ji} - \alpha_{ji}$ step. The rate function of any complex reaction for the jth reaction step is shown in Eq. (3) in which backward reaction rate is subtracted from the forward reaction rates.

$$R_j(s) = k_s^+ \prod_{i}^{k} s_i^{\alpha_i} - k_s^- \prod_{i}^{k} s_i^{\beta_i}, \quad j = 1, ...m \tag{3}$$

Here s_i are the concentrations of participating species A_i, where s is representing concentrations vector and $k(T)$ are reaction rate constants depending on temperature. The stoichiometric vectors $\eta_j = \left[\lambda_{j1}, ..., \lambda_{jk}\right]$ and reaction rate function is:

$$\Upsilon(s) = \dot{s} = \sum_{j=1}^{m} \eta_j R_j(s) \tag{4}$$

For a microscopic solution, reduction of the system is necessary when the degree of freedom is more than three because the solutions are only visualized in two or three dimensions. The law of mass conservation is:

$$Ms = C \tag{5}$$

In Eq. (5), M,s and C represents the molecular matrix, column vector of concentrations, and matrix of constants, respectively. For the key components $N_{kc} = N_c - rank(M)$, where N_{kc} and N_c are the number of key components and the number of components, respectively [12]. Applying equilibrated parameters in Eq. (5) transforms the remaining components into key components. Eventually, the system of Eq. (4) can be written in reduced form with "d" number of decreasing species as:

$$\overset{*}{\Upsilon}(s^*) = \sum_{j=1}^{d} \eta_j R_j(s^*) \tag{6}$$

Lyapunov function G is used in phase space to stabilize the equilibrium point. The equilibrium point lies on approximate curve adding shift vector we will move towards the next point. The dependency of SQEM condition $G \rightarrow \min$ is as follows:

$$\begin{aligned}
&s_{n+1} = s_n + \delta s_n, && where \quad \delta s_n = \sum_i \nu_i p_i \\
&\sum_{i=1}^{r} \left\langle \tau_j, \rho_i \right\rangle \upsilon_i = -\left(\tau_j, \Delta G(x)\right), \forall j = 1, \ldots r-1 && where \quad G = \sum_{i=1}^{k} \left[\ln\left(\frac{s_i}{s_i^{eq}}\right) - 1 \right] \\
&\sum_{i=1}^{r} (m, \rho_i)\upsilon_i = \psi^2, && where \quad \psi = 10^{-3}
\end{aligned} \tag{7}$$

Dimensions of SQEM are defined as $d < k - rank(M)$ participating k species in the reaction mechanism. A scalar product is defined as:

$$\langle \Omega_1, s \rangle = s_1, \ldots, \langle \Omega_k, s \rangle = s_k \tag{8}$$

where Ω_k are showing the slowest eigenvectors of Jacobian J at the equilibrium point?

$$J = \frac{\partial \Upsilon}{\partial s} \tag{9}$$

For further extension, every next point is used as an equilibrium point. The approximated solution curve can be found by solving Eq. (7). The ILDM is found by using the reduced system (6) where the Jacobian J^* of reduced species is:

$$J^* = \frac{\partial \Upsilon^*}{\partial s^*} \tag{10}$$

Schur decomposition is used for the partition J^*, which contains slow vectors in matrix P as:

$$P = DTD^{\bullet} \tag{11}$$

$D^{\bullet}$, T and D are the transition matrix, conjugate transposition, and upper triangular matrix. To eliminate fast trajectories, the product $D^{\bullet}\Upsilon^*(s^*)$ has set equal to zero.

$$D^{\bullet}\Upsilon^*(s^*) = 0 \tag{12}$$

This led to the construction of a 1-D ILDM in mathematical form.

2.2 A multi-step mechanism

A complex reaction with three steps, including six chemical species, is discussed in detail to understand the formation of sulfuric acid. In which oxidation of Sulfur dioxide is performed and consequently sulfuric acid is formed which is an aqueous solution [17]. In environmental chemistry this reaction is very important, due to the formation of acid rain in industrial process, or the combustion of fossil fuels Sulfur dioxide released. This complex reaction is:

$$\begin{aligned} S + O_2 &\underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} SO_2 \\ 2SO_2 + O_2 &\underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} 2SO_3 \\ SO_3 + H_2O &\underset{k_3^-}{\overset{k_3^+}{\rightleftharpoons}} H_2SO_4 \end{aligned} \tag{13}$$

In the system (13), stoichiometries in chemical reactions are mentioned in column vectors. Here, three column vectors are given which represents the coefficients of reactants and products in a balanced chemical equation as:

$$S_1 = \begin{bmatrix} -1 \\ -1 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, S_2 = \begin{bmatrix} 0 \\ -1 \\ -2 \\ 2 \\ 0 \\ 0 \end{bmatrix}, S_3 = \begin{bmatrix} 0 \\ 0 \\ 0 \\ -1 \\ -1 \\ 1 \end{bmatrix}$$

The rate expressions for every basic reaction step is expressed as follows:

$$\begin{aligned} \mathrm{R}_1(\mathrm{s}) &= \mathrm{k}_1^{+} s_1 \mathrm{s}_2 - \mathrm{k}_1^{-} \mathrm{s}_3 \\ \mathrm{R}_2(\mathrm{s}) &= \mathrm{k}_2^{+} s_2 s_3 s_3 - \mathrm{k}_2^{-} \mathrm{s}_4 \mathrm{s}_4 \\ \mathrm{R}_3(\mathrm{s}) &= \mathrm{k}_3^{+} s_4 \mathrm{s}_5 - \mathrm{k}_3^{-} \mathrm{s}_6 \end{aligned} \tag{14}$$

where $s_1 = [S], s_2 = \left[O_2\right], s_3 = \left[SO_2\right], s_4 = \left[SO_3\right], s_5 = \left[H_2O\right], s_6 = \left[H_2SO_4\right]$.

And k_1^+, k_1^-, k_2^+, k_2^-, k_3^+, k_3^-, k_4^+ *and* k_4^- are the rate coefficients depending on temperature T for the mechanism (13). By using the law of mass action, stoichiometric matrix can be expressed as follows:

$$\begin{bmatrix} 101101 \\ 022314 \\ 000022 \end{bmatrix} \begin{bmatrix} \mathrm{s}_1 \\ \mathrm{s}_2 \\ \mathrm{s}_3 \\ \mathrm{s}_4 \\ \mathrm{s}_5 \\ \mathrm{s}_6 \end{bmatrix} = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} \tag{15}$$

For each participating species in the chemical reaction its elemental composition is necessary, which gives the information about the elements present in every species and what are their quantities [18]. Molecular matrix for system (13) is given in Table 1.

Arbitrarily, parameters are selected for the equilibrium point as well as for forward rate constants, while the backward rate constants can be calculated by applying law of mass action:

$$s_1^{eq} = .5, \mathrm{s}_2^{eq} = .1, \mathrm{s}_3^{eq} = .1, \mathrm{s}_4^{eq} = .4, \mathrm{s}_5^{eq} = .2, \mathrm{s}_6^{eq} = .1$$

$$\mathrm{k}_1^{+} = 0.5, \mathrm{k}_2^{+} = 1, \mathrm{k}_3^{+} = 1.5$$

System (13) has three steps with six chemical components, and the rank of the molecular balancing matrix is three. That's why a system can be reduced to three key species s_2,s_4 and s_6. The constants s_1, s_2 and s_3 in the system are evaluated through the use of arbitrarily equilibrated parameters in Eq. (15). Hereafter, the remaining components s_2, s_4 and s_6 are transformed into key components by using the values of constants s_1, s_2 and s_3 the Eq. (15). The microscopic solutions of the

Table 1 Molecular matrix for system (13)

	S	O	H
S	1	0	0
O_2	0	2	0
SO_2	1	2	0
SO_3	1	3	0
H_2O	0	1	2
H_2SO_4	1	4	2

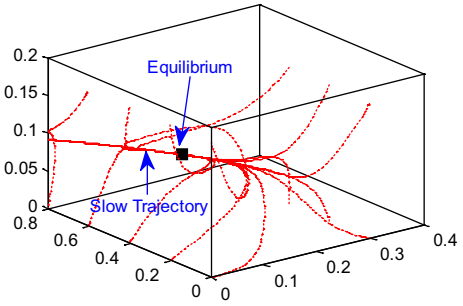

Fig. 1 solution pathways of reduced species for complex model (13)

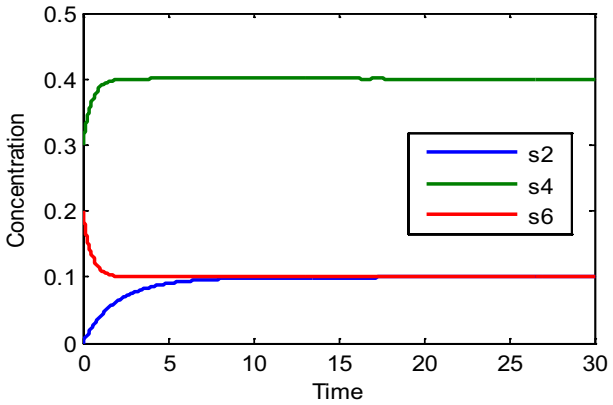

Fig. 2 Steady-state behavior of reduced species s_2, s_4 and s_6 in complex reaction

reduced key species can be found by solving the reduced system (15). These solutions are instrumental to showing an invariant region within the system.

Along this region, solutions achieved by model reduction techniques SQEM and ILDM are graphically resented. Within this invariant region, the solutions through model reduction techniques, such as SQEM and ILDM, are plotted and analyzed to assess their validity and how well they match the system's behavior. The solutions pathways for a system of reduced species are given in Fig. 1.

In a dimensional manifold, a steady state is described for the key components over the same timescale. To elaborate this, the initials for these key components are set as follows: s_2 at 0.0, s_4 at 0.3 and s_6 at 0.2. Subsequently, steady states for each of these key components are plotted, as illustrated in Fig. 2. Remarkably, it's observed that s_4 and s_6 achieve their steady state with a shorter transition period compared to s_2. Furthermore, it's noted that different initial conditions for the key components result in distinct transitional periods before reaching a steady state. Figure 2 visually demonstrates that all three species s_2, s_4 and s_6 converge toward their respective equilibrium points, each guided by its characteristic transitional period and influenced by the rate constants $k_1^+ = 0.5$, $k_2^+ = 1$, $k_3^+ = 1.5$.

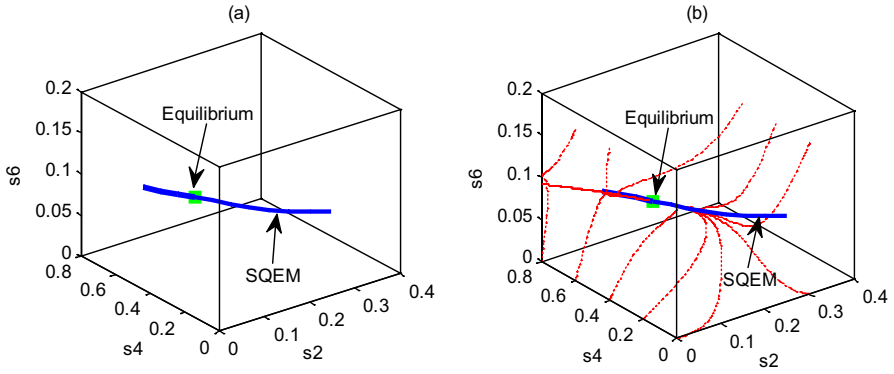

Fig. 3 **a** Solution points obtained through SQEM. **b** SQEM solution along solution trajectories in phase space

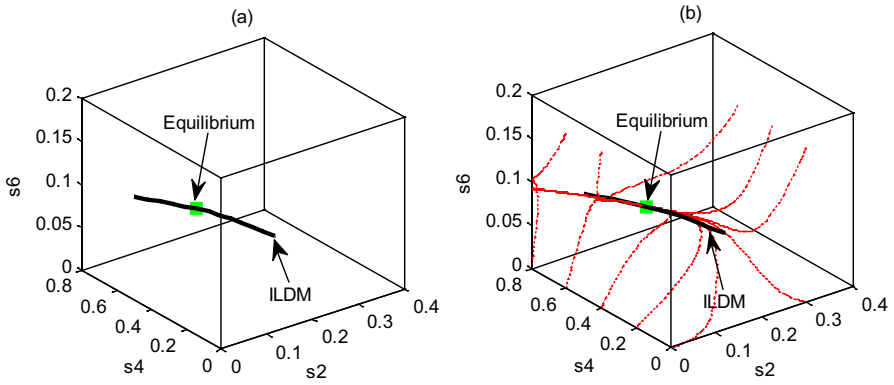

Fig. 4 **a** Solution obtained through ILDM. **b** ILDM solution along solution trajectories in phase space

Therefore, it is observed that all species start at the same time after completing their transition period and attaining an equilibrium point at different time.

3 Finding and discussions

Near to the equilibrium point, our aim is to enhance the correspondence between SIM and initial Approximation curves. Here in this article the SQEM method and ILDM method are applied separately for the invariant solutions. The phase-shifting behaviors in space R^3 are achieved at the equilibrium points and compared in terms of their solution trajectories shown in Fig. 3 for SQEM and in Fig. 4 for ILDM. For SQEM, the information on the characteristic time scales and their related components are generated together for the one-dimensional manifold. The method is used to find the initial approximated node points near

the equilibrium point. The initially approximated solution curve and the invariant region (in which solution lies) are inspected in Fig. 3a and b respectively. Similarly, in Fig. 4a and b, the solution curve obtained through ILDM method, and their solution trajectories are presented respectively. Yet, upon convergence to the equilibrium point in the forward direction, it also diverges from the invariant region. As anticipated, an approximated solution obtained through SQEM and ILDM offers a manifold near the SIM.

3.1 Comparison

Furthermore, in graphical comparison of both reduction techniques shown in Fig. 5a and b it's evident that the solution curve obtained through ILDM exhibits less deviation when compared to the solution curve obtained through SQEM. This suggests that the results achieved through ILDM are more reliable and accurate than those obtained through SQEM.

These comparative analyses provide valuable insights into the performance and reliability of different model reduction techniques, with ILDM emerging as a more dependable choice for our research purposes.

The comparison of both reduction techniques for the reduced species is mentioned in this table.

Table 2 provides the behavior of the reduced key species O_2, SO_3 and H_2SO_4 in the chemical reaction progresses. These data sets are essential for understanding the dynamic behavior of the system and for evaluating the effectiveness of different model reduction techniques, SQEM and ILDM, in predicting the system's response. The data presented in the above table shows that ILDM gives a better approximation from SQEM when these both techniques are compared for different chemical species. As each point of reduced species (O_2, SO_3 and H_2SO_4) obtained through ILDM in very close to invariant region as compared to SQEM.

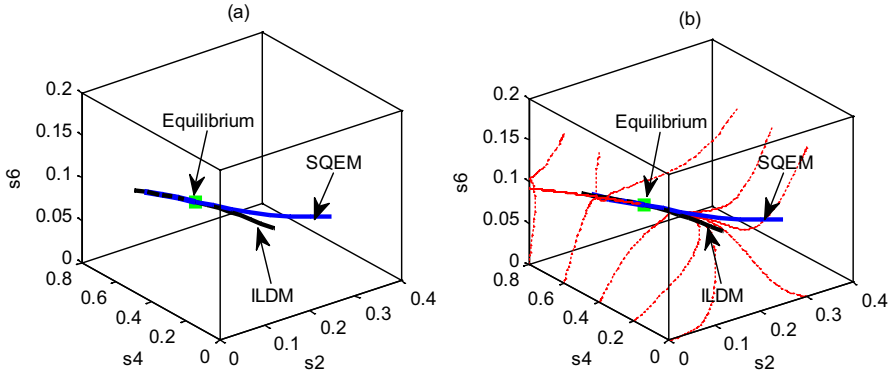

Fig. 5 **a** Comparison of solutions obtained through SQEM and ILDM. In **b** assessment of SQEM and ILDM solutions along solution paths in phase space

Table 2 comparison of some points (obtained through SQEM and ILDM) of reduced chemical species

S. no	SQEM Points for specie O_2	ILDM points for specie O_2	SQEM points for specie SO_3	ILDM points for specie SO_3	SQEM points for specie H_2SO_4	ILDM points for specie H_2SO_4
1	0.0468	0.0452	0.4919	0.4671	0.1152	0.1108
2	0.0202	0.0639	0.4612	0.4447	0.1102	0.1073
3	0.0731	0.0823	0.4305	0.4223	0.1052	0.1038
4	0.1000	0.1000	0.4000	0.4000	0.1000	0.1000
5	0.1269	0.1170	0.3695	0.3777	0.0948	0.0961
6	0.1546	0.1333	0.3394	0.3554	0.0892	0.0919
7	0.1843	0.1488	0.3098	0.3333	0.0836	0.0875
8	0.2168	0.1637	0.2815	0.3114	0.0779	0.0829

4 Conclusion

In this article, we have considered a three-step complex chemical reaction mechanism with five chemical species. Due to its complexity and higher dimension, it is impossible to get the complete solution. By applying modern model reduction schemes for the formation of H_2SO_4 on a multi-step reaction mechanism can indeed lead to low dimension which computationally efficient compared to the original mechanism. This study is first time performed computationally.

The main achievements in this study are:

- The transition time for participating species was not discussed before this, in this study the transition time is measured graphically.
- The MRTs, SQEM and ILDM are employed to get the invariant solution curves.
- Sulfur dioxide (SO_2) emission with emission norms is discussed in detail
- The invariant regions and solution pathways for the formation of H_2SO_4 in a multi-step reaction mechanism is investigated.
- Gibbs's rule has reduced the system into lower dimensions for microscopic solutions.
- It is graphically proved that slow invariant manifold obtained through ILDM is more accurate as compared to SQEM because the ILDM curve lies exactly in invariant region.
- By using this procedure, the chemists can achieve more reliable and better results.

Acknowledgements Researchers Supporting Project Number (RSP2024R33), King Saud University, Riyadh, Saudi Arabia.

Author contributions All authors reviewed the manuscript.

Declarations

Competing interests The authors declare that they have no competing interests.

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