Computational Ecology and Software, 2015, 5(3): 254-270

Article

Measuring the complex behavior of the SO_2 oxidation reaction

Muhammad Shahzad[1], **Sumaira Rehman**[1], **Rabia Bibi**[1], **Hafiz Abdul Wahab**[1], **Saleem Abdullah**[1], **Sarfraz Ahmed**[2]
[1]Department of Mathematics, HazaraUniversity, Mansehra, 21300, Pakistan
[2]Department of Mathematics, Abbottabad University of Science and Technology, Abbottabad, Pakistan
E-mail: shahzadmaths@hu.edu.pk

Received 27 April 2015; *Accepted 5 June 2015*; *Published 1 September 2015*

Abstract

The two step reversible chemical reaction involving five chemical species is investigated. The quasi equilibrium manifold (QEM) and spectral quasi equilibrium manifold (SQEM) are used for initial approximation to simplify the mechanisms, which we want to utilize in order to investigate the behavior of the desired species. They show a meaningful picture, but for maximum clarity, the investigation method of invariant grid (MIG) is employed. These methods simplify the complex chemical kinetics and deduce low dimensional manifold (LDM) from the high dimensional mechanism. The coverage of the species near equilibrium point is investigated and then we shall discuss moving along the equilibrium of ODEs. The steady state behavior is observed and the Lyapunov function is utilized to study the stability of ODEs. Graphical results are used to describe the physical aspects of measurements.

Keywords chemical kinetics; key variables; slow manifold; refinement; Lyapunov function.

Computational Ecology and Software
ISSN 2220-721X
URL: http://www.iaees.org/publications/journals/ces/online-version.asp
RSS: http://www.iaees.org/publications/journals/ces/rss.xml
E-mail: ces@iaees.org
Editor-in-Chief: WenJun Zhang
Publisher: International Academy of Ecology and Environmental Sciences

1 Introduction

Chemical materials play an effective role, not only in our daily life, such as plastics and different types of drinks, but they are also used for manufacturing defense equipments. The chemical industry is a necessary part of our development as it deals with diverse chemical reactions such as catalytic reactions, which have numerous applications in chemical industries including newly emerging applications in fine chemicals and pharmaceuticals (Roy and Chaudhari, 2005). So, the analysis of such chemical reactions has great importance. These chemical reactions vary from simple to complex depending on their corresponding nature. Gas-solid catalytic reactions are complex reactions taking place in industrial chemical processes. So it needs their theoretical and experimental investigations. Different approaches and methods have been developed for analyzing different aspects of linear chemical reactions by several researchers (Gorban and Karlin, 2003; Hangos, 2010; Roy and Chaudhari, 2005). On the other hand, due to the complexity of nonlinear chemical reactions, less attention is given to their studies. In this paper, an attempt is made to reduce the complexity and explore hidden aspects of some nonlinear chemical reactions (either fast or slow).

2 Paper Organization

Most chemical reactions have two steps in terms of the rate of occurrence i.e. fast processes and slow processes. The fast processes relax much faster than slower ones. During the relaxation, trajectories in the phase space move towards lower dimensions and converge towards the equilibrium point and after that, they start moving along it (Chiavazzo et al., 2007). This concept is represented with the help of LDM in section 2 where the system is reduced into two species in sub-section 2.2. While the steady state behavior (Bothe and Pierre, 2010; Segel and Slemrod, 1989) of the species also approaches towards the equilibrium point after completing the transition period (Fig. 3), the flow of a vector field near the equilibrium is combined with the initial approximate solution of QEM (Fig. 5).

The general idea of grid construction is given in section 3 to measure a one/higher dimension manifold. While for stability measure we use Lyapunov function is described in section 3.1.

As the solution given by QEM (Fig. 2) is far away from the exact solution shown in section 4, it is refined with the MIG (Fig. 4a, 4b). The other way left is to apply a more accurate method, for which, we apply the SQEM method (Fig. 6a) because it gives a better approximation than QEM. This is then proved by applying MIG over it and no change in the approximated 1D solution is observed (Fig. 6b). Therefore, we proceed towards the two dimensional manifold by applying the concept of SQEM and measure the 2D surface (Fig. 7). The variation in eigen values during the whole process, which is given by fast and slow processes, is calculated (Fig. 8). Finally, we conclude results in section 5.

3 Background

Different chemical reactions have different structural natures as well as distinct kinetic behaviors depending on the type of species. As a consequence of the diverse nature of chemical kinetic structures, corresponding equations can be associated with several time scales. Many physical aspects of chemical reactions are described by Slow Manifold (SM) in a better way. Thus SM plays a key role in the analysis of kinetics in chemical reactions of associated species. There are various approaches, (Chiavazzo and Karlin, 2008; Maas and Pope, 1992b; Muhammad Shahzad, 2015; Succi, 2006) which eliminate fast variables and reduce corresponding equations of the considered system into Slow Manifold (SM). Few of them are recently introduced and they are discussed in this paper in detail.

Slow Invariant Manifold (SIM) provides a simple way to study the dissipative systems of chemical kinetics and the computation of SIM after reducing the system in lower dimensions does not affect the accuracy of results.

4 Experiments

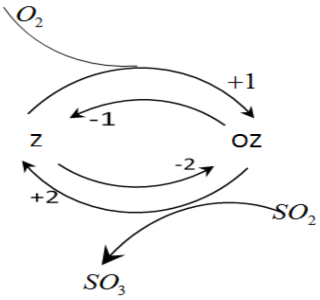

Fig a. General example of two steps, reversible reaction involving five chemical species. In the first step, O_2 react with Z (catalyst) and transformed into Z-oxide. Second step, OZ oxidizes sulphur dioxide into sulphur tri-oxide and re obtain Z. While +, - are the forward and backward reactions and 1, 2 indicates first and second step reactions.

$$\begin{aligned} &O_2 + 2Z \xrightleftharpoons[k_1^-]{k_1^+=1} 2OZ \\ &OZ + SO_2 \xrightleftharpoons[k_2^-]{k_2^+=0.5} SO_3 + Z \end{aligned} \qquad \text{(a)}$$

$$O_2 = c_1,\ Z = c_2,\ OZ = c_3,\ SO_2 = c_4,\ SO_3 = c_5$$

$$c_1^{eq} = 0.5,\ c_2^{eq} = 0.1,\ c_3^{eq} = 0.1,\ c_4^{eq} = 0.4,\ c_5^{eq} = 0.1$$

In this two-step heterogeneous nonlinear SO_2 oxidation reaction, five chemical components (O_2, Z, OZ, SO_2, SO_3) are involved, which are formed by three chemical elements (O, Z and S). All these chemical species participating in the mechanism can be divided into two groups (i.e.1: reactants and products and 2: intermediates). Intermediates are not involved in the overall reaction as they are generated in one step and consumed in another step and hence they are just a part of the cycle (Gorban and Shahzad, 2011). Now, let us explain these two steps with some details.

In the first step, oxidizing agent O_2 react together with catalyst Z and here Z is oxidized gaining oxygen atom and transformed into Z-oxide and in the second step, oxidizing agent is OZ which oxidizes sulphur dioxide into sulphur tri-oxide and we reobtain catalyst Z. Catalyst Z is only used to proceed the reaction, which takes part in the reaction, but at the end, we recovered it. Here surface intermediates are Z and OZ while the overall reaction step involved species O_2, SO_2 and SO_3.

We apply Horiuti method for finding the rate equation for reversible reaction at known rates of forward reaction as well as for obtaining equilibrium coefficient of the overall reaction (Marin and Yablonsky, 2011). It uses Horiuti numbers by means of multiplying the reaction equation in step one and step two with the Horiuti numbers 1 and 2 respectively, and afterwards, adding the equations. Every participating intermediate will be either vanished or cancelled out, i.e.

$$1.O_2 + 1(2Z) + 2.OZ + 2.SO_2 \Leftrightarrow 1(2OZ) + 2.SO_3 + 2.Z$$

$$\Rightarrow \quad O_2 + 2Z + 2OZ + 2SO_2 \Leftrightarrow 2OZ + 2SO_3 + 2Z$$

$$\Rightarrow \quad 2SO_2 + O_2 \leftrightarrow 2SO_3$$

(i.e., Intermediates are cancelled from both sides)

4.1 Linear algebra and law of mass conservation

The following relationship is valid in a regular chemical mixture:

$$A^T \eta_c = \eta_e \tag{1}$$

For a molecular matrix A^T (A transpose) of the substances O_2, Z, OZ, SO_2, SO_3 we have,

$$A^T.\eta_c = \begin{bmatrix} 2 & 0 & 1 & 2 & 3 \\ 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 \end{bmatrix}_{(3\times5)} . \begin{bmatrix} \eta_{O_2} \\ \eta_Z \\ \eta_{OZ} \\ \eta_{SO_2} \\ \eta_{SO_3} \end{bmatrix}_{(5\times1)} = \begin{bmatrix} 2\eta_{O_2} + \eta_{OZ} + 2\eta_{SO_2} + 3\eta_{SO_3} \\ \eta_Z + \eta_{OZ} \\ \eta_{SO_2} + \eta_{SO_3} \end{bmatrix}_{(3\times1)} = \eta_e$$

Consequently;

$$\begin{aligned} \eta_{t,O} &= 2\eta_{O_2} + \eta_{OZ} + 2\eta_{SO_2} + 3\eta_{SO_3} \\ \eta_{t,Z} &= \eta_Z + \eta_{OZ} \\ \eta_{t,S} &= \eta_{SO_2} + \eta_{SO_3} \end{aligned} \qquad (2)$$

where $\eta_{t,O}, \eta_{t,Z}$ and $\eta_{t,S}$ are total number of moles of O, Z and S atoms respectively. A catalytic surface reaction proceeds by means of surface intermediates, which includes active site. In this mechanism, Z and OZ are surface intermediates involving active site Z. The total amount of concentration of surface intermediates is preserved and it can be expressed as:

$$\eta_Z + \eta_{OZ} = \eta_{t,Z} \qquad (3)$$

$$\Gamma z + \Gamma_{AZ} = \Gamma_{t,Z} \qquad (4)$$

As in this case there is only one active site (i.e $N_{as} = 1 = Z$), which is part of each of intermediates (Z, OZ). In generalized form, it can be written as:

$$\sum_{i=1}^{N_{\text{int}}} b_{ik}\eta_i = \eta_{t,k} \quad \text{and} \quad \sum_{i=1}^{N_{\text{int}}} b_{ik}\Gamma j = \Gamma_{t,k} \qquad (5)$$

where b_{ik} is the number of active sites of type k which are parts of surface intermediates, i.e. η_i and Γi are the amounts (Mol) and concentrations ($molm_{cat}^{-2}$) respectively, of the *ith* surface intermediates. While $\eta_{t,k}$ and $\Gamma_{t,k}$ are the total amount (Mol) and total concentration (Mol) respectively, for active sites of type k .

Now let us check the relation between the stoichiometric matrix S and a molecular matrix A.

$$SA = \begin{bmatrix} -1 & -2 & 2 & 0 & 0 \\ 0 & 1 & -1 & -1 & 1 \end{bmatrix}_{(2\times5)} . \begin{bmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 1 & 0 \\ 2 & 0 & 1 \\ 3 & 0 & 1 \end{bmatrix}_{(5\times3)}$$

$$=\begin{bmatrix} -2+0+2+0+0 & 0-2+2+0+0 & 0+0+0+0+0 \\ 0+0-1-2+3 & 0+1-1+0+0 & 0+0+0-1+1 \end{bmatrix}_{(2\times3)} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}_{(2\times3)} \quad (6)$$

4.2 Key components

Such components, for which we need to know the concentration, by which we are able to determine the amounts of all other components, are called Key Components and they are denoted by N_{kc}. We can find the number of key components by using the following equation:

$$N_{kc} = N_c - rank(A) \quad (7)$$

N_c are the total number of components involved in the mechanism. A is a molecular matrix while its rows represent the component participates in the reaction and the columns represent the chemical elements which form components (i.e. $A(N_c \times N_e)$). Rank (A) is the rank of molecular matrix, which represent the maximum number of linearly independent variables in a row or column. It is important to note that $rank(A) \le \min(N_c, N_e)$.

4.3 Matrices and independent routes of complex reactions

The existence of intermediates in complex reaction can be affected by the stoichoimetric matrix for the intermediates (S_{int}) where the size of S_{int} matrix is ($N_s \times N_{\text{int}}$). Where,

N_s = number of steps in detailed mechanism

N_{int} = number of intermediates.

S_{int} = stoichoimetric matrix of intermediates

As intermediates are not present in the overall reaction so we have to multiply the stoichiometric matrix of intermediates and the Horiuti matrix by linear algebraic method i.e. $S_{\text{int}}(N_s \times N_{\text{int}}) \times \sigma(N_s \times N_{rr})$ where N_{rr} = number of the linearly independent reaction routes. And when we multiply σ^T and S_{int} matrices, we get matrix $\sigma^T S_{\text{int}}(N_{rr} \times N_{\text{int}})$ that is equal to zero, i.e. $\sigma^T S_{\text{int}} = 0$.

$$rank(S_{\text{int}}) = N_{\text{int}} - N_{as} \quad (8)$$

N_{as} = number of active sites in mechanism.

Also, we can find the rank (S_{int}) by the following relation,

$$rank(S_{\text{int}}) = N_s - N_{rr} \tag{9}$$

Combining relation (a) and (b) we get:

$$N_{rr} = N_s - N_{\text{int}} + N_{as} \tag{10}$$

This is the Horiuti rule. Let us consider an example (a), we have $N_s = 2$, $N_{\text{int}} = 2$. As size of

$S_{\text{int}} = N_s \times N_{\text{int}} \Rightarrow$ Intermediate matrix would be (2×2).

$$S_{\text{int}} = \begin{array}{cc} \begin{array}{cc} Z & OZ \end{array} & \\ \begin{bmatrix} -2 & 2 \\ 1 & -1 \end{bmatrix} & \begin{array}{l} Step1 \\ Step2 \end{array} \end{array}$$

Similarly, the size of the Horiute matrix (σ) = $(N_s \times N_{rr})$ implies,

$$\begin{matrix} N_s = 2 \\ Nrr = 1 \end{matrix} \Rightarrow \quad \sigma_{(N_s \times N_{rr})} = \sigma_{(2\times1)}, \quad \text{i.e. } \sigma_{(2\times1)} = \begin{bmatrix} 1 \\ 2 \end{bmatrix}.$$

As we multiply $\sigma^T S_{\text{int}}$ we take transpose on both sides

$$\sigma^T{}_{(2\times1)} = \begin{bmatrix} 1 \\ 2 \end{bmatrix}^T, \ \sigma^T = \begin{bmatrix} 1 & 2 \end{bmatrix}_{(1\times2)}, \ \sigma^T.S_{\text{int}} = \begin{bmatrix} 1 & 2 \end{bmatrix}_{(1\times2)}.\begin{bmatrix} -2 & 2 \\ 1 & -1 \end{bmatrix}_{(2\times2)} = \begin{bmatrix} 0 & 0 \end{bmatrix}_{(1\times2)}$$

$$\Rightarrow \quad \sigma^T_{(N_{rr}\times N_s)}.S_{\text{int}(N_s\times N_{\text{int}})} = \sigma^T S_{\text{int}}{}_{(N_{rr} \times N_{\text{int}})} \ .$$

4.4 Rate equation by Horiuti and Borekov

If we take SO_2 oxidation reaction, there is a two-step mechanism and all the involved components can be categorized into two groups: reactants and products. Both of them are controllable species, which means that their concentration can be set during an experiment, while it is evident that intermediates are uncontrollable species. Boreskov analyzed the oxidation of SO_2. According to both Boreskov and Horiuti, second step is the rate limiting step, which is potentially much faster than the first step, where $\sigma_{\lim} = 2$ is the Horiuti number for the rate limiting step. Boreskov used the empirical power law to define the ratio of forward and reverse rates as:

Rate equation = difference between the forward and reverse reaction rates, i.e.

$$r = \frac{r^+}{r^-} = k^+ f^+(c_r)/w \div k^{-1} f^-(c_p)/w$$

$$= k^{+} f^{+}(c_r) / k^{-1} f^{-}(c_p) \qquad \Rightarrow \; k_{eq} \, {}^{f^{+}(c_r)}\!\big/_{f^{-}(c_p)}, \qquad \frac{k^{+}}{k^{-}} = k_{eq}.$$

Hence,

$\frac{r^{+}}{r^{-}} = \left[k_{eq} \frac{f^{+1}(c_r)}{f^{-1}(c_p)} \right]^{m}$ Here m is boreskov molecularity: a number relating to the rate limiting step.

Therefore, for considering nonlinear mechanism, rate equation can be written as:

$$r = r^{+} \left\{ 1 - \left[k_{eq} \frac{f^{+1}(c_r)}{f^{-1}(c_p)} \right]^{m} \right\}.$$

5 Formalism of Invariant Manifold

The solution of the variation problem $G \to \min$ (i.e., Lyapunov function), under consideration of the constraints (2) along with the reduced decrypted form represents QEM (Chiavazzo et al., 2007). The initial approximations given by QEM or SQEM are not exact and need refinement. For this, the best available method is a 'method of invariant grids' (MIG). This is basically an iterative procedure used for the construction of slow invariant manifold (SIM). Therefore, we apply this method over the initial approximation given by QEM and SQEM and observe changes.

5.1 Grid construction

The method of invariant grid (Gorban et al., 2004) has recently been suggested by Gorban and Karlin while it was applied by many authors. The principle idea behind this construction is 'construct such an approximated grid, which lies on the invariant manifold (when refined)' with the mapping of finite dimensional grids into a dynamical phase space. Furthermore, the construction strategies have been defined in (Chiavazzo and Karlin, 2008).

By having the known node (equilibrium) the next node is calculated by the addition of shift vector; hc_p^0 i.e., $c_{p+1}^0 = c_p^0 + hc_p^0$, which also satisfies the same condition (the condition of atomic balance). For this, the best way is to express this shift vector in the form of linear combination of vectors v_i, i.e.

$$hc_p^0 = \sum_{i=1}^{z} v_i s_i \tag{11}$$

Here, s_i are the null basis given by atomic balances having dimension $z = n - l$. Thus the space perpendicular to this is given by the tangent space T that lies over the surface at each QEM node and provides the linear constraints for the system. The reason behind this partition is simple that we are looking for those points, which minimize the Lyapunov auxiliary function G.

In this way, while starting from equilibrium point c_p^0 we proceed towards the next point c_p^1 until we reach its maximum values in one direction $c_{p+1}^i > c_p^0$ while in another direction, our approach is to get the lowest value for one-dimensional curve. In simple words, a researcher can say that we are looking for, its lower and upper bound. Similarly, for a two-dimensional situation, our approach will be the same, but this time, we shall consider each grid point of the 1-D curve instead of a single point.

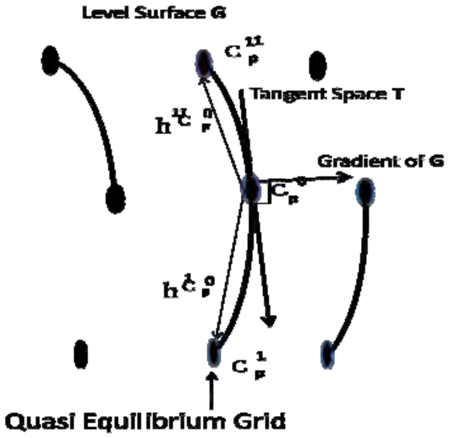

Fig.1a The general idea of grid construction starting from the equilibrium point to the next point by adding a shift vector hc_p^o in both directions.

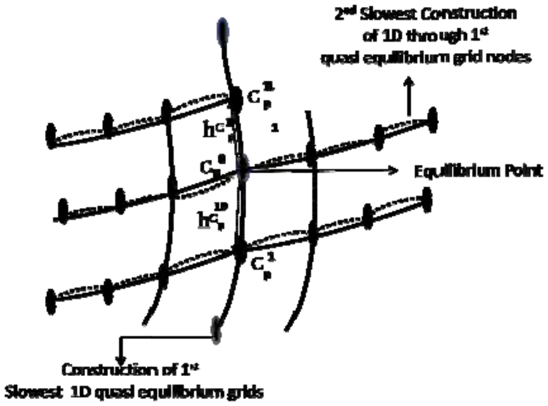

Fig.1b Extending the one dimension curve to two dimensional curve within second slowest eigen spaces when adding a new shift vector (grid points) over each grid point of one dimensional curve.

The general idea of grid construction is shown in Fig. 1 while the system will take a form (Gorban et al. 2004), i.e

$$\sum_{i=1}^{z} < t_j, s_i > \upsilon_i = -(t_j, \nabla G(c_p)), \quad \forall j = 1,...,z-1$$

$$\sum_{i=1}^{z} (v_{sl}, s_i)\upsilon_i = 0, \tag{12}$$

$$\|\mathrm{h}c_p\| = ò^2.$$

$\|\mathrm{h}c_p\|$ is Euclidean norm of shift vector, t_j is a vector of T and spaning line l lies between the two points $(t_j, A) = 0, (t_j, v_{sl}) = 0$. υ_i are unknown variables and ∇ is Gradiant. The solution of the above system at each grid point delivers two real solutions c_p^I , c_p^{II} as shown in Fig. 1 above while extending the idea for 2D, we need another directional vector v_{sl} .

As the first slow trajectory is obtained by the selection of slowest left eigenvector v_{sl}^1 at each point in the system (12), similarly with the help of second slow vector v_{sl}^2, we get another trajectory measured at each grid point of 1D curve shown in Fig. 1.

In a dynamic-system and while dealing with the system of differential equations, various types of stability may be described. Our concern for stability is closer to an equilibrium point. This may be discussed by the theory of Lyapunov. In simple words, we can say that the system starts out near an equilibrium point c_p^0 and it stays near to it forever, then it can called as Lyapunov stable. Moreover, it is asymptotically stable if all solutions that start out near c_p^0 converge towards c_p^0 .

6 Result and Discussion

In the above mechanism (a) the involved chemical components are five (i.e. $N_c = 5$) formed by the three elements (i.e. $N_e = 3$). Thus, for the system the key component (7) we have $N_{kc} = N_c - N_e = 2$. Also,

$$rank(A) \le \min(N_c, N_e) \;\; \Rightarrow \;\; rank(A) \le \min(5,3) \;\; \Rightarrow \;\; 2 \le 3.$$

While, N_{int} =2 (i.e. Z, OZ), N_{as} = 1 (i.e. Z) and N_s = 2 (i.e. two steps, reversible reaction) give the equation (8) as $rank(S_{\text{int}}) = N_{\text{int}} - N_{as} = 2-1=1$. And number of reaction routes can be found by the relation (9) as $N_{rr} = N_s - N_{\text{int}} + N_{as}$, $N_{rr} = 2-2+1$, $N_{rr} = 1$. Also, we can verify the rank of an intermediate stoichiometric matrix by relation (10) $rank(S_{\text{int}}) = N_s - N_{rr} = 2-1=1$ (Verified).

Now, we are able to reduce the system to two dimensions and for this purpose, the possible outcome can be found by the relation $X_r^n = \dfrac{n!}{r!(n-r)!}$.

As a first step we have applied the quasi equilibrium manifold method over the example (a) after reducing the species. Then, according to variation problem (Chiavazzo et al. 2007; Gorban and Karlin 2005) we have:

$$G \to min \qquad\qquad (v,c) = x \qquad\qquad Ac = \eta_e . \tag{13}$$

While under constant volume and pressure or for a (fixed) closed system, the reaction mechanism is supported by the Lyapunov function G and thus, the system will acquire the following form:

$$c_1 = x,\ \ c_2 = 2x - y - .5,\ \ c_3 = -2x + y + 0.7,\ \ c_4 = y,\ \ \ c_5 = -y + 0.5, \text{ i.e.}$$

$$G = \sum_{i=1}^{5} c_i \left(\ln\left(\frac{c_i}{c_i^{eq}} \right) - 1 \right), \quad \frac{\partial G(x,y)}{\partial y} = 0, \quad \frac{\partial^2 G(x,y)}{\partial y^2} > 0 . \tag{14}$$

y is the relation between c_1 and c_4 while $v = (1,0,0,0,0)$.

Solving the system (14), the initial approximations are shown in Fig. 2.

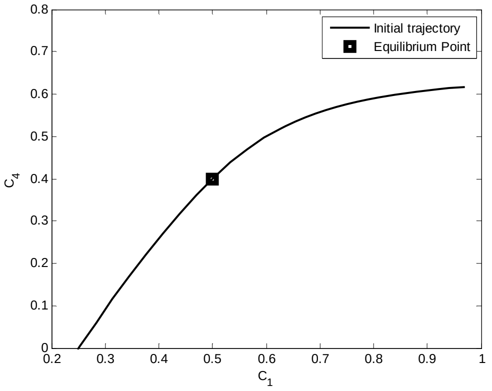

Fig. 2 The initial approximation measured by QEM in its reduced form c_1, c_4 of chemical species. A black circle shows an equilibrium point (0.5, 0.4).

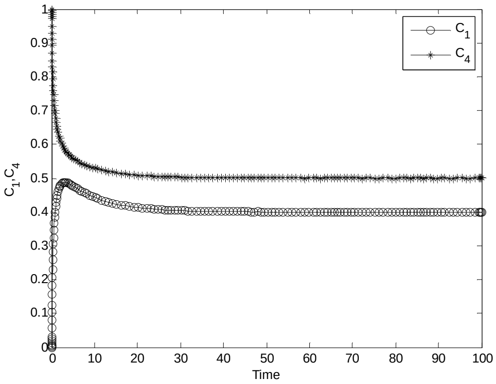

Fig. 3 After completing the transition period, the solution trajectories (c_1, c_4) goes to steady state after starting from (0,1).

The reduced mechanism with respect to c_1, c_4 also approaches towards its equilibrium point after completing its transition period as shown in Fig. 3. Similarly, other possible outcomes can be obtained and they can be shown in the same manner.

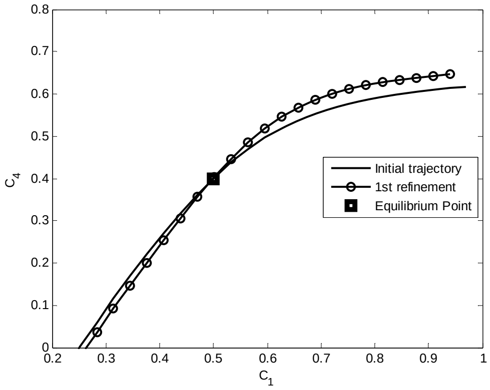

Fig. 4a Refinement of the Initial approximation (measured by QEM) using the method of the Invariant Grid at each point.

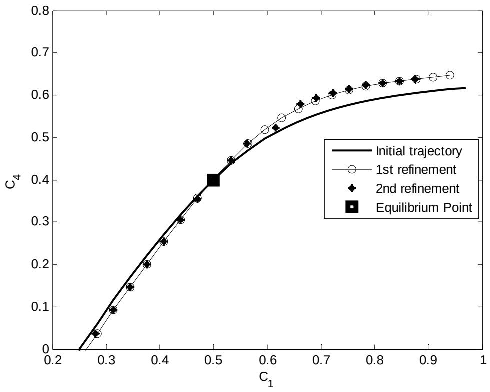

Fig. 4b The second refinement (measured by MIG) lays over the first refined trajectory. This means only first refinement gives the exact solution.

Now, refining the initial QEM in Fig. 4 the behaviour of the initial trajectories near an equilibrium point can be seen in Fig. 5.

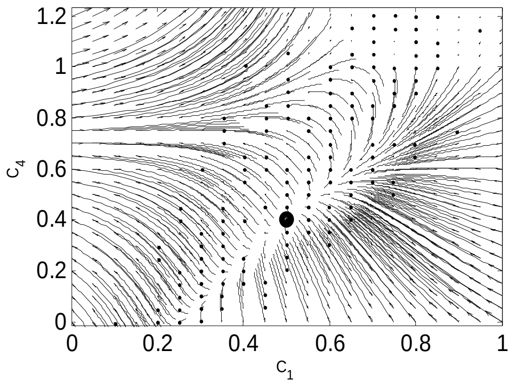

Fig. 5a Phase flow near the equilibrium point; i.e. lines along with the arrows (vector field) indicate the direction of solution trajectories converging towards the equilibrium point (black circle).

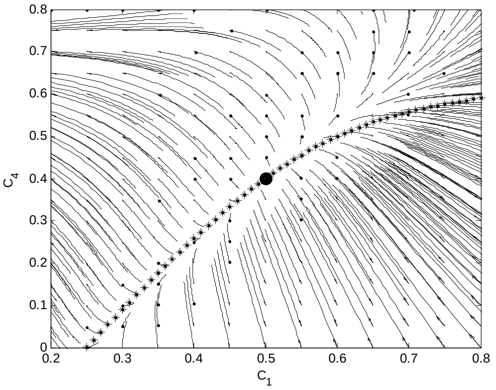

Fig. 5b The phase flow near the equilibrium point along with qem approximation passing through it, i.e (0.5, 0.4).

Now let us discuss another approximation method (SQEM), which not only reduced the system dimension, but also gave a better approximation as compared to QEM. Thus, according to system (13) and (14) we will obtain an explicit form

$$c_1 = 0.6043696330 - .3721407402y - .7599361654x\,,$$

$$c_2 = 0.7087392659 - 1.744281480y - 1.519872331x\,,$$

$$c_3 = -0.5087392659 + 1.744281480y + 1.519872331x\,,\ \ c_4 = y\,,\ \ c_5 = -y + 0.5\,,$$

after the selection of vector v (slowest left eigenvector) while Jacobin matrix J is measured at an equilibrium point

$$J = \begin{pmatrix} -.01 & -.10 & .10 & 0 & 0 \\ -.02 & -.40 & .40 & .05 & -.2 \\ .02 & .40 & -.40 & -.05 & .2 \\ 0 & .2 & -.20 & -.05 & .2 \\ 0 & -.2 & .20 & .05 & -.2 \end{pmatrix} \qquad (15)$$

delivere the first and second slowest eigenvectors, i.e.,

$$v_{sl}^1 = [\ -0.1171 \quad -0.2997 \quad 0.2997 \quad -0.2178 \quad 0.8713]$$

$$v_{sl}^2 = [0.0278 \quad 0.6522 \quad -0.6522 \quad -0.0935 \quad 0.3739] \qquad (16)$$

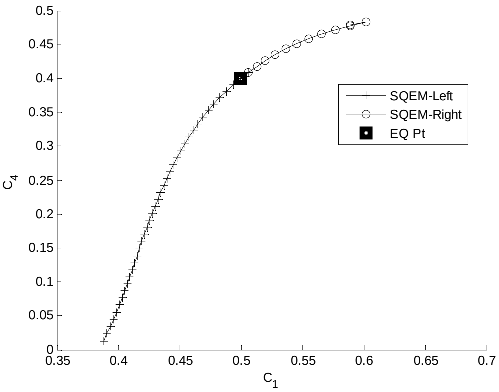

Fig. 6a Initial approximation measured by SQEM started from the equilibrium point (black circle) to both directions, using Euclidean norm $\grave{o}^2 = 10^{-2}$.

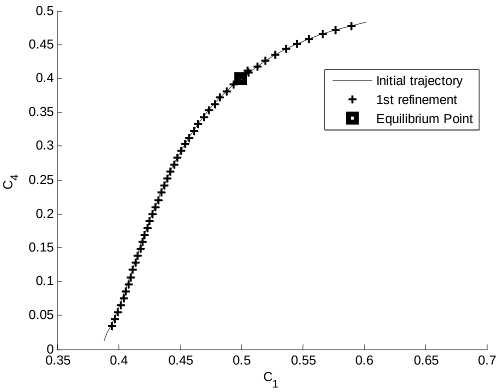

Fig. 6b Refining the initial trajectory (measured by SQEM) with the method of invariant grids shows no difference, i.e. lies over the same approximated curve.

This is now obvious from the above results (refinement Fig. 6b) that SQEM is much better than QEM approximation. Therefore, one dimensional (SQEM) curve (Fig. 6) can be extended to two dimensions by applying the method discussed in (3.1). For this purpose, we first take all the measurements (12) with respect to second slowest vector v_{sl}^2 and obtain 1D curve. Then, starting from each grid point of 1D curve, we repeat the process with vector v_{sl}^1. In this way, we obtain a surface, which lies in a phase space as shown in Fig. 7.

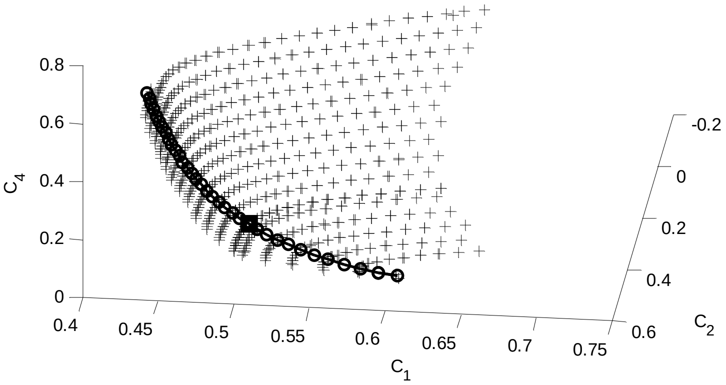

Fig. 7 Initially approximated 1D SQEM (circle line) is further extended (at some of its grid point) for 2D SQEM (black plus) in the second slowest eigen space. The equilibrium is indicated in square and the Euclidean norm in this case is $\varepsilon^2 = 0.5 \times 10^{-2}$.

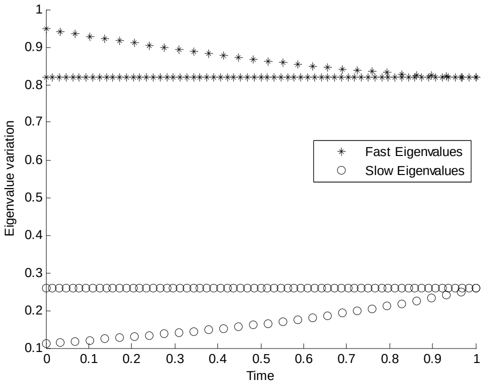

Fig. 8a Above figure indicates the variation in eigenvalues (absolute) measured at each grid point (before and after the equilibrium point) with respect to time in case of SQEM.

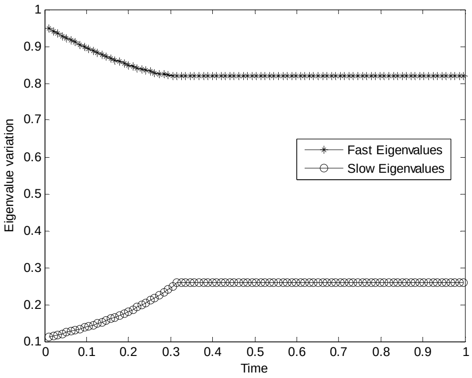

Fig. 8b Above figure indicates the variation in eigenvalues (absolute) measured at each grid point during the whole process with respect to time measured with respect to SQEM.

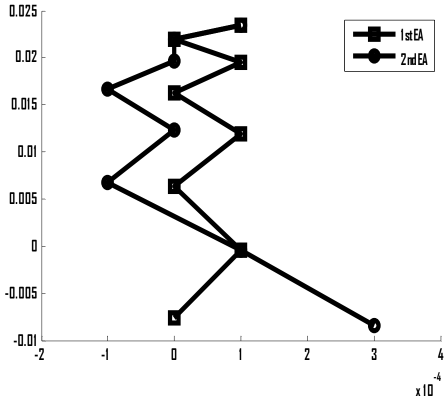

Fig. 9a. Error analysis of the Initial QEM with the MIG are shown for some grid points.

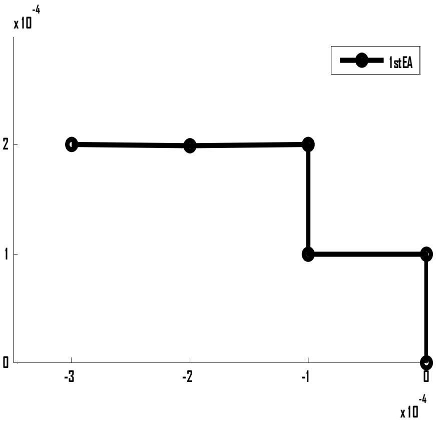

Fig. 9b. In case of SQEM the initial and the refined curve shows no difference.

Table 1 The above tables shows the difference (positive) between the initial (I) and refined (R) values of the eight grid point, which are presented in Fig.9.

Fig. 9a.	|**I-R1**|	|**I-R2**|
1	0.0234	0.0234
2	0.0219	0.0219
3	0.0195	0.0197
4	0.0163	0.0166
5	0.0119	0.0123
6	0.0063	0.0067
7	0.0004	0.0005
8	0.0076	0.0085

Fig. 9b.	1	2	3	4	5	6	7	8
|**I-R1**|	0.3606×10^{-03}	0.2828×10^{-03}	0.2828×10^{-03}	0.2236×10^{-03}	0.1414×10^{-03}	0.1414×10^{-03}	0.1000×10^{-03}	0

7 Conclusion

In this paper, the model reduction is done by employing a slow manifold approach, for which, different techniques of QEM including steady state approximation and SQEM are used. Although the Intrinsic Low Dimensional Manifold (ILDM) method, which has been presented by Maas and Pope, 1992 (Maas and Pope, 1994; Maas and Pope, 1992a; Schmidt and Maas, 1996), is one of the efficient methods used to compute SIM. But the refinement (with MIG) of the QEM, SQEM gives the same results.

The present paper gives an idea that after measuring an equilibrium point, a researcher can move to the point in a phase space near it and then towards one dimensional curve. After that, two dimensional curves can be measured while the one dimensional curve lies as a part of it.

By utilizing these approaches, five different species are reduced into some sets of two/three species, which are included in a model of a particular chemical reaction. The convergence of species also depends on their transient nature. During the implementation, it is observed that all species have a property that they converge towards their equilibrium points and then move along it. The equilibrium of ODE's are stable, which is then represented by the steady state. The stability of ODE's can be measured by Lyapunov scalar function G while the variation in eigenvalues indicates our selection of slowest variation at each point. This approach can be utilized for analyzing different chemical reactions associated with species with diverse physical nature.

References

Bothe D, Pierre M. 2010. Quasi-steady-state approximation for a reaction–diffusion system with fast intermediate. Journal of Mathematical Analysis and Applications, 368(1): 120-132

Chiavazzo E, Gorban AN, Karlin IV. 2007. Comparison of invariant manifolds for model reduction in chemical kinetics. Commun Comput Phys, 2(5): 964-992

Chiavazzo E, Karlin IV. 2008. Quasi-equilibrium grid algorithm: Geometric construction for model reduction. Journal of Computational Physics, 227(11): 5535-5560

Gorban AN, Karlin IV. 2003. Method of invariant manifold for chemical kinetics. Chemical Engineering Science, 58(21): 4751-4768

Gorban AN, Karlin IV. 2005. Invariant manifolds for physical and chemical kinetics. Lecture Notes in Physics, 660: 1-489

Gorban AN, Karlin IV. 2005. Entropy, Quasiequilibrium, and Projectors Field. Springer, Germany

Gorban AN, Karlin IV, and Zinovyev AY. 2004. Invariant grids for reaction kinetics. Physica A: Statistical Mechanics and its Applications, 333: 106-154

Gorban AN, Shahzad M. 2011. The michaelis-menten-stueckelberg theorem. Entropy, 13(5):966-1019

Hangos KM. 2010. Engineering model reduction and entropy-based Lyapunov functions in chemical reaction kinetics. Entropy, 12(4):772-797

Maas U, Pope S. 1994. Laminar flame calculations using simplified chemical kinetics based on intrinsic low-dimensional manifolds. Symposium (International) on Combustion. 1349-1356, Elsevier

Maas U, Pope SB. 1992a. Implementation of simplified chemical kinetics based on intrinsic low-dimensional manifolds. Symposium (International) on Combustion: 103-112, Elsevier

Maas U, Pope SB. 1992b. Simplifying chemical kinetics: intrinsic low-dimensional manifolds in composition space. Combustion and Flame, 88(3): 239-264

Marin G, Yablonsky GS. 2011. Kinetics of Chemical Reactions: John Wiley & Sons, USA

Muhammad Shahzad MS, Muhammad Gulistan, Hina Arif. 2015. Initially Approximated Quasi Equilibrium Manifold. Journal of the Chemical Society of Pakistan, 37: 2

Roy D, and Chaudhari RV. 2005. Analysis of a gas-liquid-liquid-solid catalytic reaction: Kinetics and modeling of a semibatch slurry reactor. Ind Eng Chem Res, 44(25): 9586-9593

Schmidt D, Maas U. 1996. Analysis of the intrinsic low-dimensional manifolds of strained and unstrained flames. Modelling of Chemical Reaction Systems, Proceedings of an International Workshop, Heidelberg, Germany

Segel LA, Slemrod M. 1989. The quasi-steady-state assumption: a case study in perturbation. SIAM Review, 31(3): 446-477