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Abstract
Starting from the general idea of reaction kinetics, their classification, concentrations, and chemical equilibrium, we will focus on their activation energy and complexity arising during the chemical reaction. As in complex and higher-dimensional chemical problems, we need special arrangements, specifically, in the case when a system attains different completion paths or several routes. The stiffness of the system can be removed if we distinctly measure their available reaction routes and get a comparison between them and overall reactions. Secondly, the construction and comparison of the invariant region of the manifold based on the modern decomposition techniques in different available reaction routes allow us to discuss the dynamical properties of the system.

Keywords: chemical equilibrium, detailed mechanism, model reduction, reaction routes, invariant manifold

1. Introduction
The chemical kinetics or reaction kinetics is the branch of physical chemistry that deals with the study of chemical processes, their rates, rearrangement of atoms, the effect of various variables, the formation of intermediates, etc. In fact, the chemical kinetics is the study of different factors affecting the speed of a chemical process and gives information about the mechanism of reaction and transition states. At the macroscopic level, the chemical kinetics deals with the study of amount reacted, formed, and the rates of their formation. While at the microscopic or molecular level, we study the mechanism of a chemical reaction, i.e., atomic collision, activation energy at different stages during the reaction.

The chemical kinetics is classified into three types, mathematical, detailed, and applied kinetics, while their elementary reactions are described as unimolecular, bimolecular, and termolecular reactions.
The **mathematical kinetics** deals with the analysis of different mathematical models used in direct and inverse chemical kinetics. These models represent a set of ordinary/partial differential equations and a set of algebraic equations. Further, direct kinetic problems deal with the analysis of steady state or nonsteady state kinetic models consisting of known kinetic parameters. On the other hand, an inverse kinetic problem reconstructs kinetic dependencies and estimates their parameters based on experimental kinetic data, either steady or nonsteady state.

The construction of the mathematical model is the key part of chemical kinetics, which gives a complete description of reaction mechanism and its rates. It provides a working tool to better understand and design chemical processes, i.e., food decomposition and the complex chemistry of biological systems, etc. These models are also used in designing the fast and slow trajectories of complex chemical reactions and modification of chemical reactors to optimize product yield, more efficiently separate products, and eliminate environmentally harmful by-products.

In **detailed kinetics**, we study the reconstruction of detailed mechanism of reaction either based on kinetic or nonkinetic data. These mechanisms consist of a set of elementary steps having forward and reverse reactions along with the governing equation of mass-action law for the kinetic dependencies. In catalyst reactions, it covers the reactant, products, intermediate, surface properties, reaction steps, reaction routes, adsorption properties, etc.

The goal of **applied kinetics** is to study the kinetic dependence of the rate of chemical reactions on their involved or related conditions, i.e., temperature, pressure, concentration, and so on. This dependence can be related to a single or a series of mathematical models usually called kinetic models. These kinetic models are necessary to represent the hierarchy of models at each stage, i.e., initial, intermediate, and final levels as well as to develop an easy way for mathematical simulations of a chemical process.

The reactions in which a single molecule rearranges itself to make one or more products are called unimolecular reactions or a first-order reaction ($A \rightarrow B$), like radioactive decay in which particles are emitted from a single atom. The reactions in which two molecules take part to form a product are called bimolecular reactions or second order ($2A \rightarrow B$ or $A + B \rightarrow C$), like cycloaddition reaction. The reactions in which three particles collide at the same place and time to form a product are called termolecular reactions or third order ($3A \rightarrow B$ or $A + 2B \rightarrow C$). The third-order reactions are not very common as all the three reactants must have to collide simultaneously to form a product.

The chemical reactions in which the reactants are in the same phases are called homogeneous reactions, i.e., the reaction between two gases, two solids, or two liquids. Let us consider a reversible chemical reaction represented as

$$
\sum_i a_{pi}A_i \xrightleftharpoons[k_i^–]{k_i^+] \sum_i b_{pi}B_i
$$

(1)

here $A_i$ and $B_i$ are the reactants and products, $k_i$ is the rate constants for forward $k_i^+$ and backward directions $k_i^–$ (that does not depend on the initial concentration of the reactants and
products but it does depend on the temperature), and $\rho = 1, \ldots, m$ are the reaction numbers, while the stoichiometric coefficients $a_{\rho i}, b_{\rho i}$ are the nonnegative integers.

The reactions in which the reactants are in different phases and their rates are affected by surface areas are called heterogeneous reactions, i.e., the reaction between gases and liquids, solids and liquids, etc. As in the case of gas solid catalytic reactions, reactants at elementary steps will be gas phase component or surface intermediate. Thus, Eq. (1) can now be written as

$$
\sum_i a_{\rho i} A_i + \sum_j a_{\rho j} X_j \xrightarrow{k_+} \sum_i b_{\rho i} B_i + \sum_j b_{\rho j} Y_j
$$

(2)

here again $A_i$ and $B_i$ are the reactant and products in the gas phase and $X_j$ and $Y_j$ are the surface intermediate. In a more typical form, it can be written as $aA + \sum_j a_{\rho j} X_j \xrightarrow{k_+} \beta B + \sum_j b_{\rho j} Y_j$.

With an assumption that $a$ and $\beta$ are either zero or one, it implies that only one molecule in an elementary reaction from the gas phase reacts or zero at all.

The concentration of the involved species can be measured as (single step reaction):

<table>
<thead>
<tr>
<th>At initial space:</th>
<th>$a$</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>time $t &gt; 0$:</td>
<td>$(a-x)$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

The reaction rates measured on either side are $k^+(a-x)^{\alpha i}$ (forward rate of reaction) and $k^- (x)^{\beta i}$ (backward rate of reaction) and the product formation is the difference between the rate of forward and backward reactions, i.e.,

$$
\frac{dx}{dt} = k^+_i (a-x)^{\alpha i} - k^-_i (x)^{\beta i}.
$$

(3)

The equilibrium is a dynamical process, and when a system goes to an equilibrium, the left-hand side will become equal to the right-hand side, i.e., $\frac{dx}{dt} = 0$

$$
k^+_i (a-x)^{\alpha i} - k^-_i (x)^{\beta i} = 0,
$$

(4)

while the conversions of products to reactants and reactants to products are still going on, although there is no net change in the number of reactant and product molecules.

According to Le-Chatelier’s principle, if a system at equilibrium state is disturbed by an external force, then the system tries to offset the force and attains a new position.

The system becomes complex when a reaction undergoes more than one pathways when more than one products are formed from the same reactants or different reactants produce the same products. Such types of reactions are called parallel reactions or side reactions, i.e.,
Here $a$ is the initial concentration of the species $A$ and after some time $t > 0$, it dispersed into $C$ and $D$. Similarly, sometimes it happens that different chemical species give the same products:

\[
\begin{align*}
\frac{n_1}{k_1} & : C \xrightarrow{(a-x)^{n_1}} A \\
\frac{n_2}{k_2} & : D \xrightarrow{(a-x)^{n_2}} D
\end{align*}
\]

or a system is reversible at different stages. In all these cases, we need to follow all their paths to get the detailed mechanisms:

\[
\begin{align*}
\frac{n_1}{k_1} & : C \xleftarrow{(a-x)^{n_1}} C \\
\frac{n_2}{k_2} & : D \xleftarrow{(a-x)^{n_2}} D
\end{align*}
\]

The rate of reaction ($W_p(c)$) is proportional to the number of collisions per unit time between the reactants but only a small fraction of the total is effective, i.e., not every collision between the reactants gives the result.

There may be a few reasons behind its ineffectiveness [1], i.e.:

1. The reactant molecules may attain insufficient energy ($< E_{\text{Act}}$, i.e., activation energy, J/mol) at different stages during the reaction.
2. The molecules may not get aligned properly or orientate during the collision (depending upon the geometry of the particles and kind of reaction that is taking place), etc.

If $Z$ is the effective collision in which molecules have energy $\geq E_{\text{Act}}$, then

\[
Z_E = \frac{Z_0 e^{E_{\text{Act}}/RT}}{RT},
\]

and $e^{E_{\text{Act}}/RT}$ gives the fraction of collisions with energy $\geq E_{\text{Act}}$.

In a complex chemical reaction, the reactant molecules (intermediates, complex $\Theta$) pass through different transition states due to their bond breaking and energy redistribution factors. Here the species stays for a very short period, usually called transition period of activated complex (where the hidden reactions between the chemical species are still going on very fast).
The energy required to pass the reactant $E_R$ to activated complex $E_Θ$ is called activation energy or energy of activation $E_{Act} = E_Θ - E_R$. It may be supplied in any form, mechanical, chemical, or thermal, to enable the reactant to convert into the product, i.e.,

$$\sum_{i=1}^{N} \alpha_S A_i \Rightarrow E_{Act}^F \Rightarrow \sum_{i=1}^{N} \beta_S A_i$$  \hspace{1cm} (6)

The activation energy during the forward $E_{Act}^F$ and backward $E_{Act}^B$ reactions must be the same or different depending on the type of reactions. In thermos, the neutral reaction and $\Delta H = 0$, the energy of activation in both the directions are same. While in endothermic reactions, $E_{Act}^F > E_{Act}^B$, holds and in exothermic reactions, $E_{Act}^F < E_{Act}^B$. It is also understood that the higher the activation energy, the slower the reaction.

The activated complex is a separate entity and there exists an equilibrium between reactants (products, under reversible reactions) and activated complex (Figure 1). Thus, a reaction mechanism can be defined as

$$\sum_{i=1}^{N} \alpha_S A_i \rightleftharpoons \Theta_i \rightleftharpoons \sum_{i=1}^{N} \beta_S A_i$$  \hspace{1cm} (7)

But still, there is some activation going on between the activated complexes $\Theta_i^R$, i.e.,

$$\Theta_i^R : \Theta_i^P = \Theta_i^P.$$

Therefore, a complete complex chemical reaction mechanism can be defined as $\sum_{i=1}^{N} \alpha_S A_i \rightleftharpoons \Theta_i^P \Rightarrow \sum_{i=1}^{N} \beta_S A_i$.

![Figure 1. A complex reaction mechanism involving energy barriers and transition states.](http://dx.doi.org/10.5772/intechopen.70502)
In case of reversible complex chemical reactions,
\[ \sum_{i=1}^{N} \alpha_S A_i \Leftrightarrow \Theta^{\pi} \Leftrightarrow \sum_{i=1}^{N} \beta_S A_i \] (8)

The concentration of activated complex can thus be obtained by applying the equilibrium conditions, i.e.,
\[ [\Theta^{\pi}] = k^{\pi} \sum_{i=1}^{N} \alpha_S A_i \] (9)

where \( \pi \) refers to the activated complex.

2. Reaction rate

A stoichiometric vector \( \gamma_{\rho} \) of the reaction mechanism (1) is an \( n- \) dimensional vector with coordinates \( \gamma_{\rho i} = \beta_{\rho i} - \alpha_{\rho i} \) that is, “gain minus loss” in the \( \rho \)th elementary reaction. In matrix form, it takes a form
\[ S = \begin{bmatrix} \gamma_{\rho 1} & \gamma_{\rho 2} & \cdots & \gamma_{\rho i} \end{bmatrix} \] (10)

The chemical composition of the substances is given by the molecular matrix \( M \), with the element \( m_{ij} \) as a number of atoms of the \( j \)th element in the \( i \)th component. \( M \) is a \((N_c \times N_e)\) matrix, while \( N_c \) is the number of reacting components lying in the mixture consisting of \( N_e \); the chemical elements and the law of conservation of atoms say
\[ Mn_c = V_c \text{ (constant vector).} \] (11)

The total number of any moles of \( c_i \) atoms can be measured by using the relation
\[ M^T n_c = n_e \] (12)

Here, \( M^T \) is the transposed molecular matrix and \( n_c \) and \( n_e \) are the component amount (mol) and the amount of the chemical elements (mol) in the column vector form.

The dynamics of the involved concentration species can be measured when we measure the rate of formation of the products or deformation and disappearance of the reactants.

Finally, the rate of reaction will take a form
\[ X(c) = \dot{c} = \frac{dc}{dt} = S_{\rho} W_{\rho}(c) \] (13)

Here \( W_{\rho}(c) \): \( W_{\rho}(c) = k_{T}(T) \prod_{i} c_i^{n_i} \) is the reaction rate function of the \( \rho \)th step (i.e., the difference between the rate of forward \( W_{\rho}^{+}(c) \) and backward \( W_{\rho}^{-}(c) \) reactions).
3. Linear algebra and graph theory

In chemical engineering, the mathematical methods of graph theory have found wide applications in complex chemical reactions and in a sequence of uni (or multi) or parallel reacting events. A graph is a combination of nodes (points) and edges (lines) [2], while a cyclic graph involves finite sequences of edges with the single node (from where it begins and ends).

Similarly, related to any combination of reaction, a tree can be defined as a sequence of noncyclic graph edges. In a spanning tree, certain intermediate may form from other intermediates after a sequence of transformations but does not agree to counter any two reactions with the same step (e.g., +1 and −1) nor two reactions started with the same intermediates (e.g., −1 and +2, or +1 and −3).

Spanning trees can be described in terms of “forward” (generated by a sequence of forwarding reactions), “backward” (generated by a sequence of reverse reactions), and “combined” spanning trees (generated by a sequence of both forward and backward reactions). A single-route, n-steps reaction mechanism has \( N_{\text{int}} \) (intermediates) nodes, such as \( N_{\text{int}} = N_{s} = N \). The total numbers of spanning trees are \( N^{2} \) in any reaction, while the forward \( N^{f} \) and backward \( N^{b} \) spanning trees are \( N^{c} \) and the numbers of combined spanning trees are

\[
N^{c} = N(N - 2) = N^{2} - 2N
\]  

In a chemical reaction, the overall reaction can be found by multiplying the reactions with certain coefficients, the so-called Horiuti numbers \( \sigma \), and then adding the results. While the relation between \( \sigma \) and \( N_{\text{int}} \) is

\[
\sigma N_{\text{int}} = 0
\]  

Horiuti number allows us to distinguish the short-lived intermediate and long-lived components, i.e., to eliminate the intermediates using an RREF of the stoichiometric matrix \( S \), the intermediates must be listed first, not last. Then the rows in which all intermediates vanish provide a basis for the overall reactions [2].

The numbers of key components \( N_{kc} \) are given by the equation

\[
N_{kc} = N_{c} - \text{rank}(M)
\]  

and the number of key components equals the number of key reactions. Also, the number of key components + number of nonkey reactions = number of reactions

In Figure 2, their curves represent two different solution curves of their respective reaction routes lying at different phase space, i.e., one lies in 2D while the second lies within 3D.

Now the question arises, if a complex reaction adopts different completion routes before giving the product, then how can one relate (or distinguish) such available routes and why they are important to be measured?

For this, the reaction route \( N_{rr} \) of the system can be measured as
whereas, $N_i$ is the number of steps in the detailed mechanism and $N_{as}$ is the number of active sites in the mechanism. Based on the molecular matrix, the molar masses of the components can be determined from the atomic masses of the elements. The product of the stoichiometric matrix $S$ and molecular matrix $M$ gives

$$SM = 0$$

To answer the second part of the above question, we need to consider all its available routes to get the detailed reaction mechanism. Then a comparison of these route solutions with the whole reaction mechanism allows us to give any concluding remarks, but we believe that the result obtained through different routes may be similar or vary depending on the type of reactions.

4. Multiroute reactions mechanism

To understand this idea, let us discern the four-step reversible complex chemical reaction [3] defined over a closed system having two available routes. The mechanism involves six chemical substances (species $C_i$) represented as (Figure 3).
While the overall reaction evolves no intermediates, i.e., \( A_2 + 2B \xrightarrow{k} 2AB \), the stoichiometric matrix (10) and molecular matrix (11) infer

\[
S = \begin{bmatrix} -1 & -2 & 2 & 0 & 0 & 0 \\ 0 & -1 & 0 & -1 & 1 & 0 \\ 0 & 2 & -1 & 0 & -1 & 1 \\ 0 & 1 & -1 & -1 & 0 & 1 \end{bmatrix}, \quad M = \begin{pmatrix} A & Z & B \\ 2 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 1 \\ 1 & 0 & 1 \end{pmatrix}
\]

(19)

Note that the relation between them is orthogonal, i.e., Eqs. (15) and (18) hold. While the stoichiometric matrix of intermediates and Horiuti matrix are \( N_{\text{int}} = 4 \), \( N_{\text{int}} = 3(Z, AZ, BZ) \), \( N_{\text{as}} = 1(Z) \),

\[
N_{\text{int}} = \begin{pmatrix} -2 & 2 & 0 \\ -1 & 0 & 1 \\ 2 & -1 & -1 \\ 1 & -1 & 0 \end{pmatrix}, \quad \sigma = \begin{pmatrix} -1 & 0 \\ 0 & 1 \\ -2 & -1 \\ 0 & 1 \end{pmatrix}
\]

Atomic balance constraints are given by Eq. (11)

\[
\begin{align*}
\eta_{t,A} &= 2\eta_{c_1} + \eta_{c_3} + \eta_{c_6} \\
\eta_{t,Z} &= 2\eta_{c_2} + \eta_{c_3} + \eta_{c_5} \\
\eta_{t,B} &= 2\eta_{c_4} + \eta_{c_5} + \eta_{c_6}
\end{align*}
\]

(20)

whereas, \( \eta_{t,A} \), \( \eta_{t,Z} \), and \( \eta_{t,B} \) are the total number of moles of \( A \), \( Z \), and \( B \) atoms, respectively.

The key components \( N_{lc} \) and reaction route \( N_{rr} \) of the system are given by Eqs. (16) and (17)

\[
N_{lc} = N_c - \text{rank}(M) = 6 - 3 = 3.
\]
This means we can reduce this system into three components

\[ N_{rr} = N_s - N_{int} + N_{as} = 4 - 3 + 1 = 2. \]

Hence, this reaction mechanism has two independent routes \( N_{rr} \). Also, when we multiply step-1 and step-3 by its Horiuti numbers, all the intermediates vanished and we get an overall reaction. The same is the case with steps 1, 2, and 4. The dimension of these two routes can be determined by their respective Horiuti numbers. Sets of Horiuti numbers for the first route and second route are \((1,0,0,2)\) and \((1,2,2,0)\), respectively. This implies both the routes are nonlinear.

First-route: two-step mechanisms (Figure 4).

Second-route: three-step mechanisms (Figure 5).
5. The measuring methods

The kinetic equations of the above reaction mechanism (R-1) can be measured by using Eq. (13)

$$
\frac{d}{dt} \begin{bmatrix} c_{A2} \\ c_B \\ c_{AB} \\ c_Z \\ c_{AZ} \\
\end{bmatrix} = \begin{bmatrix}
-k_1 c_1 c_2^2 - k_1 c_3^2 \\
-k_2 c_2 c_4 - k_2 c_2 c_5 - 2k_1 c_1 c_2^2 + 2k_1 c_3^2 \\
-k_4 c_2 c_4 + k_2 c_2 c_5 + 2k_1 c_1 c_2^2 - 2k_1 c_3^2 \\
-k_3 c_2 c_4 + k_2 c_2 c_5 \\
k_2 c_2 c_4 - k_2 c_2 c_5 
\end{bmatrix}
$$

while \( N_s=2, N_{int}=2(Z,AZ), N_{in}=1(Z), \) and a reaction route \( N_{tr} \) is 1.

A reduced form of the system (R-1) can be achieved by using the Eqs. (12) and (13). While initial parameters are defined as

\( c_1^{\text{in}} = 0.5, c_2^{\text{in}} = 0.1, c_3^{\text{in}} = 0.1, c_4^{\text{in}} = 0.4, c_5^{\text{in}} = 0.1, k_1^{\text{in}} = 1, k_2^{\text{in}} = 0.5. \)

Similarly, (R-2) implies that we can reduce this system into three components, while \( N_s = 3, N_{int} = 3(Z,ZO,ZCO), N_{in} = 1(Z), \) and \( N_{tr} = 1. \)

Thus, a single reaction route is available. The kinetic equations for the involved species are given by Eq. (13)

$$
\frac{d}{dt} \begin{bmatrix} c_{A2} \\ c_B \\ c_{AB} \\ c_Z \\ c_{AZ} \\
\end{bmatrix} = \begin{bmatrix}
-k_1 c_1 c_2^2 - k_1 c_3^2 \\
2k_2 c_2 c_4 - 2k_2 c_2 c_5 - k_2 c_2 c_5 + k_2 c_4 - 2k_1 c_1 c_2^2 + 2k_1 c_3^2 \\
-k_4 c_2 c_4 + k_2 c_2 c_5 + 2k_1 c_1 c_2^2 - 2k_1 c_3^2 \\
-k_3 c_2 c_4 + k_2 c_2 c_5 + k_2 c_2 c_5 - k_2 c_4 \\
-k_3 c_2 c_4 + k_2 c_2 c_5 + k_2 c_2 c_5 - k_2 c_4 \\
k_3 c_3 c_4 - k_3 c_3 c_6 
\end{bmatrix}
$$

By using Eqs. (12) and (13), a system can be reduced into three numbers of species and their initial parameters are defined as

\( c_2^{\text{in}} = 0.1, c_3^{\text{in}} = 0.1, c_3^{\text{in}} = 0.4, c_4^{\text{in}} = 0.5000000000, c_5^{\text{in}} = 0.5000000000, c_6^{\text{in}} = 0.5000000000, c_7^{\text{in}} = 0.5000000000, c_8^{\text{in}} = 0.5000000000. \)

\( k_1^{\text{in}} = 1, k_2^{\text{in}} = 0.5, k_3^{\text{in}} = 0.5. \)

Figures 6 and 7 clear the idea of the slow invariant manifold (SIM), i.e., decomposing the system into their fast and slow motion. Their solution trajectories (during their relaxation time) quickly move toward the low-dimensional manifold and after that start moving along it [4–13]. That is the easy way of getting an idea of the SIM. Otherwise, by using the different available methods of SIM, i.e., [14–27] we will get their initial approximations lying on it or near to it. For comparison, we refer the readers to [28].
Figure 6. The behavior of the reduced species $c_1$ and $c_4$ near the equilibrium point (square). While their solution trajectories approaching toward the equilibrium (during their path) give the region where slow invariant manifold (SIM) lies.

Figure 7. The equilibrium point (square) and behavior of the reduced species near to it.
6. The routes comparison

In Figure 9, the curves lie in the plane $c_1$ and $c_4$ are not the projected image of the above curves. Instead, it is the behavior of the species measured near the equilibrium point in the first reaction route mechanism, whose $N_k = 2$. Similarly, the above lines describe the behavior of the

![Figure 8](image1.png)

**Figure 8.** Two-dimensional view of both the reaction routes solutions and both squares represent their equilibrium point.

![Figure 9](image2.png)

**Figure 9.** First-route vs. second-route. The three-dimensional view of both the reaction routes solutions and both squares represent their equilibrium point.
species near the equilibrium point measured in second reaction route mechanism, whose $N_{ic} = 3$. Note that its invariant region and equilibrium point exactly lie over the invariant region of the first route, i.e., Figures 8, 9.

Now, the overall reaction mechanism involves no intermediate, and the variations of the concentration of involved chemical species are given in Figure 10.

7. Summary

In this chapter, both the physicochemical conceptual assumptions (used for species behavior and activated complex) and a set of mathematical tools (for their dynamical behavior and simplification) are presented. Mathematically, simplification can be done by “model reduction,” that is, the rigorous way of approximating and representing a complex model in simplified form.

Here, we have considered a complex problem having a common step: conferred their available routes then allied graphically. Although we have not applied any numerical or analytical technique to measure the SIM but one can easily examine (by applying such techniques) that their solution trajectories will also lie in the same invariant regions that can also be correlated with each other and even with the whole reaction mechanism.

Thus, the idea initiated here can easily be correlated with the method used for the construction of slow manifold in a complex chemical reaction based on the decomposition techniques of entropy maximum along with certain constraints (lies on the manifold or given by slowest eigenvectors) at the equilibrium point. This will allow us to bring together different available mathematical ideas and methods, commonly used to transform the complex chemical problems from one way to the other, to enhance progress in understanding.
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