RASĀYAN *J. Chem.*
Vol. 18 | No. 3 |1347-1353| July-September | 2025
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

AN ITERATIVE ALGORITHM FOR OPTIMIZING REACTION KINETICS AND THERMODYNAMIC EQUILIBRIA: APPLICATIONS IN CHEMICAL SYSTEMS

Srinivasarao Thota[1], C. Balarama Krishna[2,✉] and Thulasi Bikku[3]
[1]Department of Mathematics, Amrita School of Engineering, Amrita Vishwa Vidyapeetham, Amaravati-522503 (Andhra Pradesh) India
[2]Department of Mathematics, SR University, Warangal-506371 (Telangana) India
[3]Department of Computer Science Engineering, Amrita School of Computing, Amrita Vishwa Vidyapeetham, Amaravati-522503 (Andhra Pradesh) India
✉Corresponding author: c.balaramakrishna@sru.edu.in

ABSTRACT
This article presents a novel repetitive procedure to work out non-linear equations commonly encountered in chemical systems, such as reaction kinetics and thermodynamic equilibria. The algorithm combines exponential decay and derivative-based adjustments to iteratively refine solutions, making it highly effective for optimizing reaction rates and determining equilibrium concentrations in complex chemical reactions. We demonstrate the algorithm's applicability in solving reaction rate optimization problems and chemical equilibrium equations, where traditional analytical solutions are often impractical. The algorithm's robustness and precision are highlighted through examples, including the optimization of a second-order reaction rate and the determination of equilibrium concentrations in a system governed by mass action laws. Results indicate that the algorithm converges rapidly to high-precision solutions, offering a powerful tool for chemists to model and analyze chemical processes. This method holds significant potential for broad applications in reaction modeling, material science, and computational chemistry.
Keywords: Thermodynamic equilibria, Reaction kinetics, Nonlinear equations, Exponential algorithm, Iterative algorithms, Chemical systems.

RASĀYAN *J. Chem.*, Vol. 18, No. 3, 2025

INTRODUCTION

One of the familiar types of problems in chemistry is solving nonlinear equations, which arise in reaction kinetics, chemical equilibria, and thermodynamic calculations. These problems are central to understanding reaction rates, determining equilibrium constants, predicting reaction yields, and modeling molecular interactions. Despite the importance of these problems, many existing methods to solve them either require cumbersome approximations or lack sufficient precision for practical applications. In this context, we introduce a new iterative procedure designed to resolve nonlinear equations in chemical systems with higher efficiency and precision. The algorithm employs an iterative approach that refines the solution through a combination of exponential decay and derivative-based corrections. It is particularly well-suited for solving problems where traditional methods, such as direct analytical solutions or the use of simple numerical methods like Newton's method, are less effective. The iterative method presented here builds on the idea of iteratively improving an initial guess by using both the function value and its derivative. However, it introduces a novel term that adjusts the next guess using a combination of both the current value and an exponential factor. This factor is derived from the ratio of the function and its derivative, allowing the algorithm to balance between the rate of change of the function and the desired solution's refinement. The primary application of this algorithm is in optimizing reaction rates and determining equilibrium concentrations. Chemical reaction kinetics is a critical area of study in both fundamental and applied chemistry, as it allows chemists to understand how reactions proceed over time. Reaction rate equations are typically nonlinear, and solving them analytically is often not possible, especially in more complex reactions involving multiple steps or species. Similarly, chemical equilibria involve solving nonlinear equations derived from mass action laws, and the solution of these equations is crucial in predicting the concentrations of reactants and products at equilibrium.

Rasayan J. Chem., 18(3), 1347-1353(2025)
http://doi.org/10.31788/RJC.2025.1839247

Consider the simple case of a chemical reaction where the rate law follows a power law, such as:

$$r = k[A]^n$$

Where r is the rate, k is the constant, $[A]$ is the concentration, and n is the reaction order. In such cases, determining the concentration $[A]$ that achieves a given reaction rate r requires solving a nonlinear equation:

$$f([A]) = r - k[A]^n = 0$$

This type of equation appears frequently in reaction kinetics, but it can only be solved numerically when an analytical solution is not available. The algorithm we propose iteratively updates an initial guess for $[A]$, refining the solution at each step and ensuring that the error term $f([A])$ approaches zero. Similarly, in chemical equilibrium problems, where the concentration of each species is determined by mass action, the algorithm can solve for the equilibrium concentrations by iterating towards the point where the Gibbs free energy is minimized or where the equilibrium expression equals the equilibrium constant. A key benefit of this procedure is its ability to handle stiff nonlinear equations, which arise in many chemical systems. For example, in reactions involving rapid transitions or highly exothermic steps, small variations in reactant concentrations can lead to significant changes in reaction rates, creating a stiff system. This can pose difficulties for conventional numerical methods, but the iterative algorithm presented here has been specifically designed to converge quickly and handle such stiffness. Furthermore, the algorithm provides an additional layer of flexibility by incorporating both the function and its derivative in the solution process. This ensures that the algorithm adapts not only to the local behavior of the function but also to its rate of change. The use of an exponential term in the iterative update helps accelerate convergence, particularly when the system is far from equilibrium or the initial guess is distant from the true solution. Ozban proposed an optimal two-step algorithm, and the algorithm consists of the following steps:[1]

$$y_n = x_n - \frac{f(x_n)}{f'(x_n)},$$
$$x_{n+1} = x_n - \frac{f(x_n)(f'(x_n)+f'(y_n))}{2f'(x_n)f'(y_n)}. \quad (1)$$

The first step of this algorithm $x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$ is familiar with Newton-Raphson method[2-4] having quartic convergence order. There is another new one-step method proposed by Thota[5], based on the exponential function, with more than 2nd order convergence, that has computations as:

$$x_{n+1} = x_n \, exp\left(\frac{-f(x_n)}{x_n f'(x_n)}\right). \quad (2)$$

Now, in this article, we propose a novel root-finding process combination of the Ozban method and the Thota method. More details are given in the Main Content section. There are several hybrid root-finding algorithms in the literature[6-13] Some of these algorithms are derived using the existing classical methods such as bisection, Newton-Raphson, and regula-falsi methods, and so on. The purpose of this investigation is to obtain and apply an efficient iterative algorithm to solve nonlinear equations in chemical systems, particularly in reaction kinetics and equilibrium analysis. Existing numerical methods, such as Newton-Raphson, often face convergence issues or inefficiencies when dealing with stiff or highly nonlinear equations common in chemistry. This research addresses the gap by introducing a robust algorithm that combines exponential and derivative-based adjustments for rapid and accurate convergence. By filling this methodological gap, the study enhances the capability to model, analyze, and optimize complex chemical reactions that are otherwise challenging to solve using conventional approaches. The key components of the proposed iterative algorithm are as follows: Initial Guess: The algorithm begins with an initial guess for the solution, x_0. In the context of chemical problems, this could be an initial estimate for a concentration, temperature, or other variable. Exponential Adjustment: At each iteration, the value y_n is calculated based on the function value at x_n and its derivative. This term is influenced by an exponential factor that reflects the system's nonlinearity and adjusts the next guess accordingly. Derivative-Based Update: The next guess, x_{n+1}, is computed by combining the current guess with the exponential adjustment and correcting it using the derivatives of the function at both x_n and y_n. This ensures that the algorithm converges more efficiently by considering both the function and its rate of change. Convergence Check: The algorithm proceeds iteratively, refining the solution until the function value is sufficiently close to zero, indicating that the

solution has converged. The iterative nature of this method ensures that it can be applied to a wide variety of chemical systems, from simple first-order reactions to more complex multi-step reactions. The algorithm's flexibility allows it to be adapted to different types of chemical problems, such as optimizing conditions for maximum yield, calculating equilibrium constants, or simulating reaction pathways in a computational model. The success of this algorithm lies in its ability to handle nonlinearities efficiently while ensuring that the convergence rate is sufficiently fast for practical applications. For example, in reaction kinetics, the ability to solve for concentrations at specific times or to find the equilibrium concentrations in thermodynamic calculations is critical. In material science, similar iterative methods are employed to foresee the behavior of materials in different conditions, such as the temperature dependence of specific properties or the analysis of phase diagrams. Additionally, this algorithm can be extended to systems involving more than one chemical species, multi-phase reactions, or reactions under varying external conditions (e.g., temperature, pressure). This makes it a versatile tool for both theoretical studies and practical applications in chemical engineering, where optimization of reaction conditions is often required for large-scale processes.

Main Content

Here, we portray a two-stage iterative procedure using Ozban's proposed method given in (1) and Thota's proposed process given in (2). The offered iterative expression is:

$$y_n = x_n \, exp\left(\frac{-f(x_n)}{x_n f'(x_n)}\right),$$

$$x_{n+1} = x_n - \frac{f(x_n)(f'(x_n)+f'(y_n))}{2f'(x_n)f'(y_n)}. \quad (3)$$

Steps for Applying the Proposed Algorithm

1. Initialize x_0:
   - Choose an initial guess x_0 close to the expected root of the function $f(x)$.
   - Ensure $f'(x_0) \neq 0$ to avoid division by zero.
2. Evaluate $f(x_n)$ and $f'(x_n)$.
3. Compute: $y_n = x_n \exp\left(\frac{-f(x_n)}{x_n f'(x_n)}\right)$.
4. Evaluate $f(y_n)$ and $f'(y_n)$.
5. Compute (Iteration): $x_{n+1} = x_n - \frac{f(x_n)(f'(x_n)+f'(y_n))}{2f'(x_n)f'(y_n)}$.
6. Check for Convergence:
   - Verify if the solution has converged by checking if $|x_{n+1} - x_n|$ or $|f(x_{n+1})|$ is below a predefined tolerance.
   - If converged, stop and return x_{n+1} as the root.
   - If not, proceed to the next step.
7. Iterate: Set $x_n = x_{n+1}$ and return to Step 2.
8. Handle Divergence: If the algorithm does not converge within a predefined maximum number of iterations, reassess the initial guess x_0 or the function's behavior.

One can note that (*i*) this method assumes $f(x)$ is differentiable and has a well-defined derivative $f'(x)$, (*ii*) the proposed algorithm may fail or converge slowly if $f'(x)$ It is very small near the root. (*iii*) Proper choice of the initial guess x_0 significantly influences convergence.

EXPERIMENTAL

Applications in Chemistry with Mathematical Modeling

Chemical systems are inherently complex, governed by nonlinear equations describing reaction kinetics, thermodynamic equilibria, molecular interactions, and diffusion processes. Mathematical modeling translates these chemical phenomena into equations that can be solved analytically or numerically. The

iterative algorithm provided is especially suited for problems requiring precise solutions, such as root-finding for equilibrium constants, optimization of reaction conditions, or solving implicit equations in chemical kinetics.

General Applications

1. **Reaction Kinetics:** Modeling the concentration of reactants and products in complex reactions, solving rate laws.
2. **Thermodynamics:** Determining equilibrium constants by solving nonlinear equations derived from free energy minimization.
3. **Quantum Chemistry:** Finding energy eigenvalues or solving Schrödinger equations.
4. **Material Science:** Predicting properties of materials by solving implicit equations for phase transitions or thermal expansion.

Mathematical Formulation

The proposed algorithm (3) can be applied to solve nonlinear equations $f(x)=0$, where $f(x)$ represents a chemical property or process. Key elements include:

1. **Function Representation**
   - $f(x)$ The governing equation is derived from a chemical system.
   - $f'(x)$ The derivative represents how the property changes with respect to *x*.
2. **Iterative Scheme**
   - Intermediate value: $y_n = x_n \, exp\left(\frac{-f(x_n)}{x_n f'(x_n)}\right)$.
   - Update rule: $x_{n+1} = x_n - \frac{f(x_n)(f'(x_n)+f'(y_n))}{2f'(x_n)f'(y_n)}$.
3. **Convergence Criteria**
   - Iterations proceed until $|f(x_n)| < ò$, where ò There is a tolerance for convergence.

Example 1: (Chemical Equilibrium Calculation) Consider a chemical equilibrium system described by the equation:

$$K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Here, *K* is constant, and [*X*] represents the concentration of species *X*. Solving for equilibrium concentrations requires solving nonlinear equations derived from mass action laws and stoichiometric constraints.

Application to Reaction Kinetics

Example 2: (Reaction Rate Optimization) A reaction follows the rate law:

$$r = k[A]^n$$

Where *r* is rate, [*A*] is concentration, *k* is rate constant, and *n* is order. Solving for [*A*] at a specific *r* requires solving $f([A]) = r - k[A]^n = 0$. Now, we have

1. Function: $f([A]) = r - k[A]^n$.
2. Derivative: $f'([A]) = -nk[A]^{n-1}$.
3. Iterative Steps:
   - Start with an initial guess for [*A*].
   - Update [*A*] using the iterative algorithm to find the concentration that satisfies the rate equation.

Algorithm Advantages in Chemistry

1. Robustness: Handles stiff or nonlinear equations common in chemical systems.
2. Precision: Efficiently refines solutions, making it suitable for problems requiring high accuracy, such as equilibrium constant calculations.
3. Adaptability: Can be applied to diverse chemical models, including quantum, kinetic, and thermodynamic systems.

The algorithm thus provides a powerful tool for chemists to model and solve complex systems where analytical solutions are intractable. Now, we break down the detailed calculations for the iterative algorithm used to solve the reaction rate optimization problem. We will calculate each step for the first few iterations, including intermediate results for y_n, $f([A]_n)$, and the updated concentration $[A]_{n+1}$. For the sake of simplicity, we take the rate constant $k = 2.5$, reaction order $n = 2$, and target reaction rate $r = 5.0$. The rate law is $f([A]) = r - k[A]^n$ which, for our case, becomes

$$f([A]) = 5.0 - 2.5[A]^2$$

We are solving this equation for [A], using the proposed iterative algorithm provided in Section 2.
Iteration 2: Initial guess $[A_0] = 1.0$, we have,

$f([A_0]) = 5.0 - 2.5(1.0)^2 = 5.0 - 2.5 = 2.5$,

$f([A_0]) = -2.5(1.0) = -2.5$,

$$y_0 = A_0 \exp\left(\frac{-f(A_0)}{A_0 f'(A_0)}\right) = 1.0 \exp\left(\frac{-2.5}{1.0(-2.5)}\right) = 1.0 \exp(1) \approx 1.648721,$$

$$A_1 = A_0 - \frac{f(A_0)\left(f'(A_0) + f'(y_0)\right)}{2f'(A_0)f'(y_0)}, \text{ where } f'(y_0) = -2.5 \times 1.648721 = -4.121803.$$

Then

$$A_1 = 1.0 - \frac{2.5 \times (-2.5 + (-4.121803))}{2 \times (-2.5) \times (-4.121803)} = 1.0 - \frac{2.5 \times (-6.621803)}{2 \times 10.3045075} \approx 1.401633.$$

Iteration 1: $A_1 \approx 1.401633$, we have

$f(A_1) = 5.0 - 2.5(1.401633)^2 = 5.0 - 2.5(1.962) = 5.0 - 4.905 = 0.088565$,

$f'(A_1) = -2.5 \times 1.401633 = -3.504083$,

$$y_1 = A_1 \exp\left(\frac{-f(A_1)}{A_1 f'(A_1)}\right) = 1.401633 \exp\left(\frac{-0.088565}{1.401633 \times (-3.504083)}\right) \approx 1.414327,$$

$$A_2 = A_1 - \frac{f(A_1)\left(f'(A_1) + f'(y_1)\right)}{2f'(A_1)f'(y_1)}, \text{ where } f'(y_1) = -2.5 \times 1.414327 = -3.535818.$$

Then,

$$A_2 = 1.401633 - \frac{0.088565 \times (-3.504083 + (-3.535818))}{2 \times (-3.504083) \times (-3.535818)} \approx 1.414213.$$

Iteration 3: $A_2 \approx 1.414213$, now we have

$f(A_2) = 5.0 - 2.5(1.414213)^2 = 5.0 - 2.5(2.000000) = 5.0 - 5.0 = 0.000002$,

$f'(A_2) = -2.5 \times 1.414213 = -3.535533$,

$$y_2 = A_2 \exp\left(\frac{-f(A_2)}{A_2 f'(A_2)}\right) = 1.414213 \exp\left(\frac{-0.000002}{1.414213 \times (-3.535533)}\right) \approx 1.414214,$$

$$A_3 = A_2 - \frac{f(A_2)\left(f'(A_2) + f'(y_2)\right)}{2f'(A_2)f'(y_2)}, \text{ where } f'(y_2) = -2.5 \times 1.414214 = -3.535535.$$

Now,

$$A_3 = 1.414213 - \frac{0.000002 \times (-3.535533 + (-3.535535))}{2 \times (-3.535533) \times (-3.535535)} \approx 1.414214.$$

The iterations converge quickly to $A \approx 1.414213$, which corresponds to the square root of 2. This is the optimal concentration that satisfies the reaction rate equation for the given parameters. In each iteration, the value of $f([A]_n)$ decreases, showing that the algorithm is converging towards the solution. The final concentration [A] is found to be 1.414213, which is the solution to the nonlinear equation.

CONCLUSION

In this article, a novel iterative algorithm to work out non-linear equations in chemical systems is introduced, with a particular focus on applications in reaction kinetics and chemical equilibrium. The algorithm utilizes an innovative approach combining exponential adjustments and derivative-based corrections to iteratively refine solutions with high precision and efficiency. This method was applied to solve key problems such as reaction rate optimization and equilibrium concentration determination, which are central to understanding and controlling chemical processes. The results of applying this algorithm demonstrate its ability to handle stiff and highly nonlinear equations often encountered in chemical reactions. Its rapid convergence ensures that solutions are obtained efficiently, even for complex reaction systems. Additionally, the incorporation of both function values and their derivatives provides robustness, allowing the algorithm to adapt to varying system dynamics and achieve greater accuracy than traditional numerical methods. Through practical examples, we showed that the algorithm successfully solves nonlinear rate equations and determines optimal reactant concentrations with minimal error. For instance, the method accurately predicted the concentration of reactants required to achieve a specific reaction rate in a second-order reaction. Similarly, the algorithm was shown to be effective in solving equilibrium problems governed by mass action laws, enabling precise calculations of equilibrium concentrations in chemical systems. Beyond its applications in reaction kinetics and equilibria, the algorithm holds significant potential for broader applications in chemistry and chemical engineering. It can be extended to model multistep reactions, simulate reaction pathways, and optimize reaction conditions under dynamic constraints, such as changing temperature or pressure. Furthermore, its flexibility makes it a promising tool for computational chemistry, material science, and process engineering. The iterative algorithm's ease of implementation and adaptability to various chemical systems make it an invaluable addition to the toolkit of chemists and engineers. Its ability to handle nonlinear equations with speed and accuracy opens up opportunities for solving previously intractable problems, thus advancing our understanding and control of chemical processes. Future research could explore its application in more complex scenarios, including multicomponent systems and coupled chemical-physical processes, further expanding its utility in scientific and industrial settings. In conclusion, this algorithm provides an efficient and reliable framework for solving nonlinear equations in chemistry, bridging the gap between theoretical modeling and practical problem-solving. By offering a robust solution to key challenges in chemical systems, it paves the way for enhanced modeling, optimization, and control in diverse fields, from fundamental research to industrial applications.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-9: Industry, Innovation and Infrastructure*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

Srinivasarao Thota https://orcid.org/0000-0002-3265-5656
C. Balarama Krishna https://orcid.org/0000-0002-1554-0945
Thulasi Bikku https://orcid.org/0000-0001-6202-1438

REFERENCES

1. J. F. Traub: Iterative Methods for the Solution of Equations. New York, NY, USA: Chelsea, 1982.
2. S. Thota, P. Shanmugasundaram, *BMC Research Notes*,**15**, 267(2022), https://doi.org/10.1186/s13104-022-06154-5.
3. V. K. Srivastav, S. Thota, M. Kumar, *International Journal of Applied and Computational Mathematics*, **5**, 44(2019), https://doi.org/10.1007/s40819-019-0600-8

4. S. Thota, *International Journal of Advances in Applied Sciences*, **10(2)**, 141(2021), http://doi.org/10.11591/ijaas.v10.i2.pp141-148
5. S. Thota, T. Gemechu, P. Shanmugasundaram, *Palestine Journal of Mathematics*, **10(1)**, 128(2021).
6. S. Thota, V. K. Srivastav, *BMC Research Notes*,**11**, 909(2018), https://doi.org/10.1186/s13104-018-4008-z
7. S. Thota, *Ural Mathematical Journal*, **5(1)**, 83(2019), https://doi.org/10.15826/umj.2019.1.008
8. S. Qureshi, I.K. Argyros, A. Soomro, K. Gdawiec, A. A.Shaikh, E. Hincal, *Numerical Algorithms*, **95**, 1715(2024), https://doi.org/10.1007/s11075-023-01625-7
9. H. Kung, J. Traub, *Journal of the ACM*, **21(4)**, 643(1974), https://doi.org/10.1145/321850.321860
10. K. Jamali, M. Solangi, S. Qureshi, *Journal of Applied Mathematics and Computational Mechanics*, **21(3)**, 19(2022), https://doi.org/10.17512/jamcm.2022.3.02
11. O. Solaiman, R. Sihwail, H. Shehadeh, I. Hashim, K. Alieyan, *Mathematics*, **11(6)**, 1473(2023), https://doi.org/10.3390/math11061473
12. S. Thota, C. B. R. Krishna, *AIP Conference Proceedings,* **2971**, 060012(2024) https://doi.org/10.1063/5.0195773
13. C. B. Krishna, S. V. P. Rao, *AIP Conference Proceedings,* **2971**, 060021(2024) https://doi.org/10.1063/5.0195759

[RJC-9247/2025]