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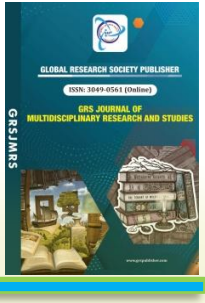

Comparative Analysis of the Relationship between Rate Constant and Half-Life in Zero-, First-, and Second-Order Chemical Reactions

K.S. Pritikkasri[a] and S. Sivamani[b,c,*]

[a]Junior Director, SKPT Academic and Research Services, Namakkal, India

[b]Department of Engineering and Technology, University of Technology and Applied Sciences, Salalah, Oman

[c]Director, SKPT Academic and Research Services, Namakkal, India.

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Corresponding Author:
S. Sivamani*

Abstract: The relationship between reaction rate constant and half-life is fundamental to understanding chemical kinetics and predicting reaction behaviour. Although expressions describing half-life for zero-, first-, and second-order reactions are well established, comparative visualization across different reaction orders is seldom presented. This study provides a mathematical comparison of half-life as a function of reaction rate constant and the corresponding inverse relationship for zero-, first-, and second-order reactions. Calculations were performed using standard integrated rate equations assuming identical initial reactant concentration of 1 M. The resulting plots demonstrate that half-life decreases nonlinearly with increasing rate constant for all reaction orders. At any given rate constant, second-order reactions exhibit the longest half-life, followed by first-order and zero-order reactions. Conversely, the rate constant decreases with increasing half-life, producing inverse relationships characteristic of each kinetic order. The results emphasize the distinct kinetic behaviour associated with reaction order and provide a useful graphical framework for interpreting experimental kinetic data. These findings may serve as references for professionals involved in reaction kinetics.

***Keywords**: Chemical kinetics, Half-life, Rate constant, Reaction order.*

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Introduction

Chemical kinetics is the branch of physical chemistry that investigates the rates of chemical reactions and the factors governing the transformation of reactants into products. Unlike chemical thermodynamics, which determines whether a reaction is energetically feasible, chemical kinetics focuses on how rapidly a reaction proceeds and the pathways through which it occurs [1]. The rate of a chemical reaction is influenced by several variables, including reactant concentration, temperature, pressure, catalysts, solvent properties, and the intrinsic nature of the reacting species. Understanding reaction kinetics is fundamental to the design, optimization, and control of chemical processes because it enables prediction of reaction behaviour under varying operating conditions [2]. Consequently, kinetic analysis has become indispensable in chemical engineering, environmental engineering, pharmaceutical sciences, materials science, food processing, and biochemical engineering [3].

Among the fundamental kinetic parameters, the half-life (t½) occupies a central position because it provides a simple and intuitive measure of reaction duration [4]. Half-life is defined as the time required for the concentration of a reactant to decrease to one-half of its initial value. Since this parameter directly reflects the persistence of reactants, it serves as a convenient indicator for comparing reaction speeds across different systems [5]. Half-life has extensive practical significance beyond chemistry. In medicine and pharmacokinetics, it determines the duration of drug activity and guides dosage intervals to maintain therapeutic concentrations [6]. In nuclear science, radioactive half-life is used to estimate isotope decay, geological dating, and radiation safety [7]. Environmental scientists employ half-life to evaluate the persistence of pesticides, pollutants, and contaminants in soil, water, and air, thereby assessing environmental risks and remediation strategies [8]. Similarly, in food engineering, half-life is applied to quantify nutrient degradation, vitamin stability, and shelf-life prediction, while chemical industries use half-life for reactor design, catalyst performance evaluation, and process optimization. These widespread applications demonstrate that half-life is not merely a theoretical kinetic parameter but also a practical decision-making tool across numerous scientific and engineering disciplines [9,10].

While half-life is the most widely recognized measure of reaction persistence, another useful concept is the fractional-life, which refers to the time required for a reactant concentration to decrease to any specified fraction of its initial value rather than exclusively one-half [11]. Examples include quarter-life (time to reach one-fourth of the original concentration), tenth-life, or any arbitrary fractional reduction relevant to a particular application. Fractional-life provides greater flexibility when monitoring reactions that require specific conversion levels, such as pollutant removal, pharmaceutical degradation, food preservation, or industrial conversion processes. Unlike half-life, which represents a fixed 50% reduction, fractional-life allows researchers and engineers to tailor kinetic analysis to operational requirements [12]. Consequently, fractional-life offers a broader framework for understanding reaction progress, whereas half-life remains the standard benchmark because of its simplicity and universal acceptance [13].

Another fundamental parameter in chemical kinetics is the reaction rate constant (k), which quantitatively describes the intrinsic speed of a chemical reaction under specified conditions [14]. The rate constant incorporates the effects of molecular collisions, activation energy, catalyst presence, and temperature, making it a characteristic parameter of the reaction mechanism [15]. According to the Arrhenius equation, the rate constant generally increases exponentially with temperature, resulting in shorter reaction times and reduced half-lives [16]. Larger values of the rate constant therefore indicate faster reactions, whereas smaller values correspond to slower transformations [17]. Since reaction rate constants are experimentally measurable and mathematically incorporated into integrated rate laws, they provide the foundation for predicting concentration changes with time and designing industrial reactors [18].

Equally important is the reaction order, which describes the mathematical dependence of reaction rate on reactant concentration [19]. Reaction order is determined experimentally and reflects the underlying reaction mechanism rather than the stoichiometric equation [20]. Zero-order, first-order, and second-order reactions exhibit distinctly different concentration–time relationships and consequently different half-life expressions [21]. For a zero-order reaction, the half-life is directly proportional to the initial concentration and inversely proportional to the rate constant, indicating that higher reactant concentrations prolong the reaction duration [22]. In contrast, the half-life of a first-order reaction is independent of the initial concentration and depends solely on the rate constant, making it constant throughout successive half-lives [23]. For second-order reactions, half-life depends on both the initial concentration and the rate constant; producing a more complex relationship in which reactant concentration significantly influences reaction persistence [24]. These mathematical distinctions illustrate that reaction order fundamentally controls how reaction duration changes as reactants are consumed.

The individual effects of reaction order and rate constant on half-life have been extensively established through integrated rate equations [25]. An increase in the rate constant invariably reduces the half-life because reactants are consumed more rapidly. Conversely, variations in reaction order alter the mathematical relationship between concentration and time, causing half-life to respond differently depending on the kinetic mechanism. However, in practical systems, reaction order and rate constant do not operate independently. Their interactive effect determines the overall kinetic behaviour of a reaction [26]. For example, a moderate increase in the rate constant may substantially reduce half-life for a first-order reaction but produce a different magnitude of reduction in zero- or second-order systems due to the influence of concentration-dependent terms. Understanding this interaction is therefore essential for accurately predicting reaction lifetimes, selecting operating conditions, and optimizing industrial processes where both kinetic parameters vary simultaneously.

Visualization techniques have become increasingly valuable for interpreting these multidimensional kinetic relationships [27]. Among these techniques, three-dimensional surface plots provide an effective means of simultaneously representing two independent variables and one dependent response. Surface plots have been widely adopted in engineering applications, particularly in process optimization, computational modelling, response surface methodology (RSM), machine learning, and design of experiments. They enable researchers to identify trends, interaction effects, optimum operating regions, and nonlinear responses that may not be evident from conventional two-dimensional graphs [28]. In chemical engineering, surface plots are commonly employed to evaluate reactor performance, catalyst activity, adsorption processes, wastewater treatment, corrosion inhibition, energy systems, and process parameter optimization. Their ability to visualize complex interactions makes them particularly suitable for studying the combined influence of reaction order and rate constant on half-life [29].

Previous studies and standard chemical kinetics have thoroughly established the mathematical derivation of half-life expressions for zero-, first-, and second-order reactions [30,31]. Numerous investigations have applied these relationships in pharmaceuticals, environmental degradation, radioactive decay, polymerization, catalysis, and biochemical reactions [32-34]. However, most published studies present each reaction order independently, with emphasis on analytical equations rather than integrated visualization [31,32,35]. Comparative graphical analyses that simultaneously evaluate the combined influence of reaction order and rate constant on half-life remain relatively limited [30,33,36]. Furthermore, few studies employ three-dimensional surface plots to illustrate the interaction between these kinetic variables over a continuous parameter space [34,37]. As a result, understanding of the interactive effects is often restricted to mathematical derivations instead of intuitive visual interpretation.

This limitation represents an important research gap. Although the theoretical relationships between half-life, reaction order, and rate constant are well established, there is limited visualization-based analysis demonstrating how these variables interact across a broad range of kinetic conditions. Such visualization could improve interpretation of kinetic behaviour, facilitate educational understanding, and support engineering decision-making by revealing nonlinear trends and interaction regions that may not be apparent from equations alone.

The novelty of the present study lies in integrating classical kinetic theory with modern three-dimensional graphical visualization to investigate the combined influence of reaction order and rate constant on half-life. Rather than examining each reaction order separately, this work presents a unified surface representation that highlights both individual and interactive effects of the governing kinetic parameters. The approach provides a more comprehensive understanding of reaction lifetime and offers an accessible framework for interpreting kinetic relationships relevant to research, teaching, and industrial process optimization. Therefore,

the aim of this study is to investigate and visualize the individual and combined effects of reaction order and reaction rate constant on the half-life of chemical reactions using mathematical kinetic models and three-dimensional surface analysis. The specific objectives are to: (i) Review the theoretical relationships among half-life, reaction order, and reaction rate constant based on integrated rate laws; (ii) Evaluate the influence of reaction order on half-life for zero-, first-, and second-order reactions; (iii) Examine the effect of varying rate constants on reaction half-life; (iv) Investigate the interactive influence of reaction order and rate constant on half-life using three-dimensional surface plots; and (v) Demonstrate the usefulness of surface visualization as a tool for interpreting chemical kinetic behaviour and supporting engineering applications.

Methods

Mathematical Model

Half-life expressions were obtained from the integrated rate laws for each reaction order [30,31].

For a zero-order reaction, $t_{1/2} = \frac{C_{A0}}{2k}$ (1)

For a first-order reaction, $t_{1/2} = \frac{\ln(2)}{k}$ (2)

For a second-order reaction, $t_{1/2} = \frac{1}{C_{A0}k}$ (3)

Where $t_{1/2}$ is half-life, k is rate constant, and C_{A0} is initial reactant concentration.

Assumptions

To ensure a consistent and meaningful comparison of the effects of reaction order and rate constant on half-life, several simplifying assumptions were adopted in this study. The initial reactant concentration was assumed to remain constant across all calculations to eliminate concentration-dependent variations and enable direct comparison among different reaction orders. Temperature was considered constant throughout the analysis, thereby maintaining a fixed reaction rate constant and excluding thermal effects described by the Arrhenius equation. The study further assumed ideal kinetic behavior, implying that the reactions strictly obey the integrated rate laws for zero-, first-, and second-order kinetics without deviations. In addition, no side reactions, catalyst effects, mass transfer limitations, or external influences were considered, ensuring that the observed variations in half-life were solely attributable to changes in reaction order and rate constant. These assumptions provide a simplified theoretical framework for investigating the fundamental relationships among the kinetic parameters.

Data collection and analysis

Rate constants ranging from 0.005 to 0.050 (appropriate units depending on reaction order) were selected. The corresponding half-life values were calculated using the Equations (1)-(3). Similarly, half-life values ranging from 15 to 150 min were used to calculate the corresponding rate constants by rearranging the Equations (1)-(3). The calculated values were plotted as half-life versus rate constant at various orders of reaction. Rate constant versus half-life using nonlinear trend lines to compare kinetic behaviour among reaction orders.

Surface plots

Rectangular and surface plots were plotted using Microsoft Excel 2019. A three-dimensional surface plot was generated to examine the combined influence of reaction order and rate constant on the half-life of a reaction. Reaction orders ranging from 0 to 2 and rate constants between 0.005 and 0.045 min^{-1} were considered. Half-life values were computed using the appropriate integrated rate-law equations corresponding to each reaction order and plotted as the response variable (z-axis). The resulting surface was color-coded into four half-life intervals (0–50, 50–100, 100–150, and 150–200 min) to facilitate visualization of regions with similar half-life values and to identify trends across the reaction-order and rate-constant space. The colour bands represent half-life ranges of 0–50 min (blue), 50–100 min (orange), 100–150 min (grey), and 150–200 min (yellow), illustrating how half-life changes with variations in reaction order and rate constant.

Results and Discussion

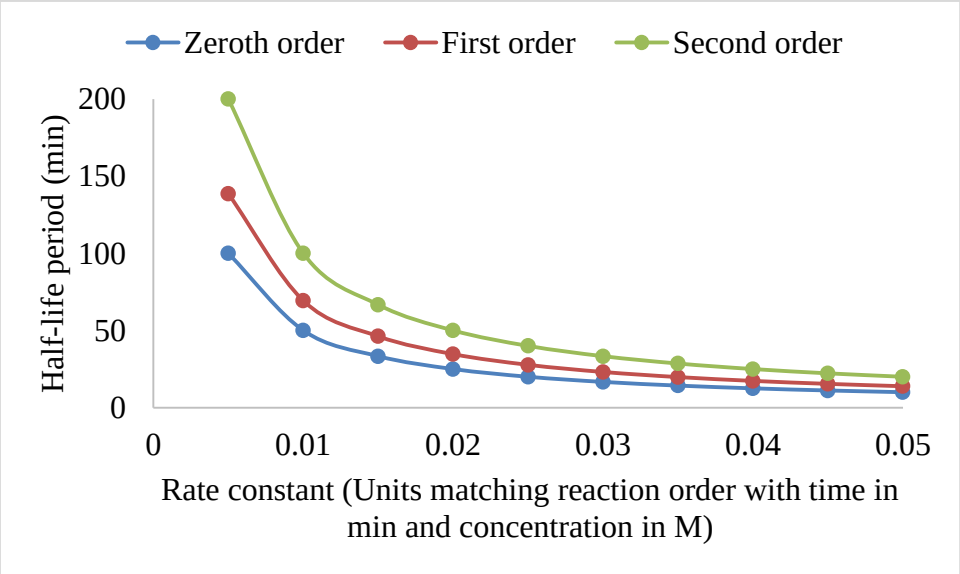

Figure 1. Effect of half-life on the rate constant for zero-, first-, and second-order reactions

Figure 1 illustrates the dependence of half-life on the reaction rate constant for zero-, first-, and second-order reactions. As the reaction rate constant increased, the half-life decreased rapidly for all reaction orders. The decline was nonlinear, showing a steep decrease at lower values of

k followed by gradual flattening at higher values [38]. At identical rate constants, zero-order reactions exhibited the shortest half-life, first-order reactions showed intermediate values, and second-order reactions possessed the longest half-life. These differences became less pronounced as the rate constant increased.

Figure 2 presents the inverse relationship between rate constant and half-life. The rate constant decreased with increasing half-life for all reaction orders, again following nonlinear inverse trends [39]. Second-order reactions consistently required larger rate constants than first-order and zero-order reactions to achieve identical half-life values. Overall, both figures demonstrate the expected inverse dependence between reaction rate constant and reaction lifetime.

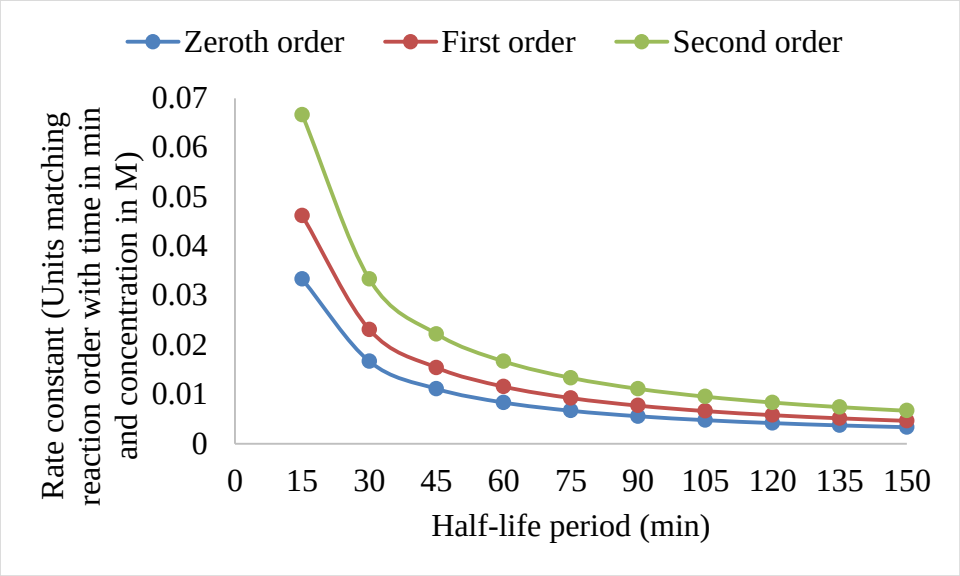

Figure 2. Effect of rate constant on half-life for zeroth-, first- and second-order reactions

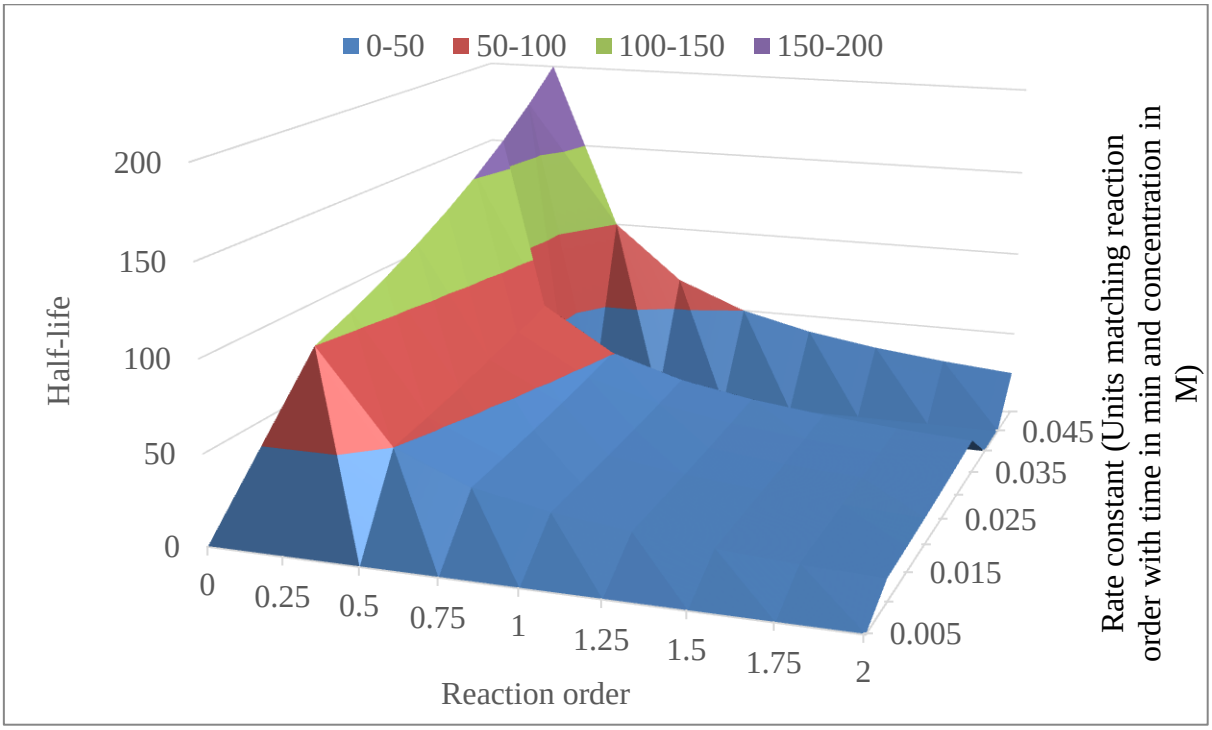

Figure 3. Three-dimensional surface plot showing the relationship between reaction order (0–2), rate constant (0.005–0.045), and the corresponding half-life (min)

The surface plot demonstrates that half-life is strongly influenced by both reaction order and rate constant (Figure 3). Lower half-life values (0–50 min; blue region) dominate at higher reaction orders and relatively larger rate constants, indicating faster reaction completion. As the rate constant decreases, half-life increases progressively, producing intermediate (50–100 min; orange) and high (100–150 min; grey) regions [40]. The highest half-life values (150–200 min; yellow) are concentrated around intermediate reaction orders (approximately 0.5–1.0) coupled with lower rate constants, where the reaction proceeds most slowly. The plot also reveals a nonlinear response, with abrupt changes in half-life occurring over relatively small variations in reaction order and rate constant.

The graphical analysis clearly demonstrates that reaction order strongly influences the relationship between half-life and reaction rate constant.

Zero-order reactions display the smallest half-life because reactant depletion proceeds at a constant rate independent of concentration. Consequently, increasing the rate constant produces a rapid reduction in reaction lifetime.

First-order reactions exhibit exponential decay, resulting in the well-known concentration-independent half-life. This characteristic explains why many radioactive decay and pharmaceutical degradation processes show constant half-lives.

Second-order reactions possess the greatest half-life due to their dependence on reactant concentration. As the concentration decreases during the reaction, the reaction slows considerably, prolonging the time required to consume half of the reactant.

The inverse plots further emphasize that relatively small changes in rate constant could substantially alter reaction lifetime, particularly at low k values. At higher rate constants, the curves gradually approach asymptotic behaviour, indicating diminishing sensitivity of half-life to additional increases in k. These graphical comparisons provide a practical framework for interpreting kinetic experiments and selecting appropriate reaction models. The figures may also serve as educational tools for illustrating the contrasting kinetic characteristics associated with different reaction orders.

The observed trends are consistent with reaction kinetics, where the half-life is inversely related to the rate constant; increasing the rate constant shortens the time required for reactant consumption. The dependence of half-life on reaction order introduces additional complexity because each reaction order follows a distinct mathematical relationship with reactant concentration. Consequently, the surface is nonlinear rather than planar, reflecting the combined effects of kinetic parameters.

The concentration of high half-life values at lower rate constants highlights the dominant influence of reaction rate on reaction persistence. In contrast, increasing the reaction order generally shifts the system toward shorter half-lives over much of the examined range, although localized peaks indicate that the interaction between reaction order and rate constant is not strictly linear. These findings emphasize that accurate estimation of both kinetic parameters is essential for predicting reaction duration, optimizing process conditions, and designing chemical or biochemical systems where reaction time is a critical performance criterion. Hence, the surface plot provides a comprehensive visualization of the interaction between reaction order and rate constant, demonstrating that higher rate constants consistently reduce half-life, while the effect of reaction order depends on its interaction with the rate constant and the underlying kinetic model.

One limitation of this study is that calculations were performed using ideal kinetic equations under constant temperature and fixed initial concentration. Real systems may deviate because of catalyst effects, competing reactions, diffusion limitations, or changing environmental conditions.

Conclusion

This study presents a comparative mathematical evaluation of the relationship between reaction rate constant and half-life for zero-, first-, and second-order reactions. The results demonstrate that:

- Half-life decreases inversely with increasing reaction rate constant.
- Rate constant decreases inversely with increasing half-life.
- Second-order reactions consistently exhibit the longest half-life.
- Zero-order reactions exhibit the shortest half-life.

The influence of reaction order is greatest at small rate constants and becomes less pronounced as the rate constant increases. These findings reinforce fundamental principles of chemical kinetics and provide a clear graphical reference for understanding how reaction order affects reaction lifetime. The presented analysis may assist researchers, educators, and students in interpreting kinetic data and selecting suitable kinetic models for experimental systems.

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