

Exploring Chemical Kinetics: Insights into Reaction Dynamics and Mechanistic Pathways

Dr. Rajesh Sihag

Head of Department, Chemistry, Maharshi Dayanand Girls P.G. College, Jhunjhunu- 333001

ABSTRACT

One of the main subfields of physical chemistry that focuses on examining the rates at which chemical transformations occur as well as the mechanisms underlying these rates is chemical kinetics. The Michaelis-Menten model for enzyme reactions, Lindemann's theory for unimolecular reactions, and Bodenstein and Lind's steady state approximation have all contributed to the field's ongoing improvement of mechanisms. Theoretical approaches like as transition state theory, Rice-Ramsperger-Kassel-Marcus (RRKM), and Marcus electrical transmission theory are used in modern advancements to determine rate constants. Depending on whether the reactions are pre-parameterized or involve direct dynamics, recent techniques use PES from quantum mechanics in conjunction with dynamics to predict reaction rates. Despite significant progress, there are still issues with handling multistep processes that involve at least one out-of-equilibrium intermediate state, as well as processes that occur in liquids and amorphous materials. With an emphasis on complexity features in contemporary theoretical chemical kinetics, this work provides a deeper comprehension of the interplay of dynamics, mechanism, and electronic structure.

INTRODUCTION

Therefore, chemical kinetics—one of the most significant fields of physical chemistry, with roots in the earliest days of scientific inquiry—is, in fact, a vital piece of fundamental equipment for figuring out the rate and mechanism of chemical processes. Since the field's inception, the identification of the precise rate constant for each elementary step has been at its core, serving as the foundation for the theories and approximations that define the discipline. For example, Lindemann discovered that activated molecules had a role in unimolecular reactions through the Lindemann mechanism, while Bodenstein and Lind worked on the steady-state approximation to simplify the computational handling of complex reaction setups. In an effort to explain multistep enzymatic reactions, the Michaelis-Menten mechanism—a model that is still in use today—further developed these ideas. Theoretical developments have also significantly improved our ability to calculate positional rate constants. While RRKM theory and Marcus theory integrated the microcanonical, pressure dependent, and electron transfer data, transition state theory (TST) emerged as a useful framework for describing the pressure independent thermal rate constants. However, thanks to contemporary quantum mechanical ideas like the Schrödinger equation and scattering theory, it is now feasible to calculate step-specific rate constants in really basic situations.

PES and dynamics can now be combined to estimate reaction rates with great accuracy thanks to advancements in recent years. In other words, PES can be computed online by changing the internal coordinates using direct dynamics techniques, or it can be derived from quantum mechanical calculations. Even while these approaches have proven effective for electrically adiabatic reactions, they are unable to handle electronically non-adiabatic processes, such as those involving UV-visible light, due to new problems. Despite these advances, certain facets of reaction mechanisms—especially in structurally disordered species—remain state-of-the-art problems in chemical kinetics. Some reactions do not lend themselves to the examination of stepwise processes, while others proceed through mechanisms that entail several steps and intermediates at energies that are out of equilibrium with the reactants and products. This work examines the present and upcoming theoretical approaches to chemical kinetics, focusing on issues of complexity. Chemical kinetics is analyzed at the molecular level by taking dynamics, processes, and electronic structures into consideration. Chemical kinetics links reaction rate to the underlying mechanistic processes and offers a highly deep perspective on how chemical systems behave.

From looking for simple processes that were similar to figuring out the energy flow limit in the molecular dissociation phase at the state level in gaseous states to investigating intricate multistep reaction mechanisms in big molecules, this field has changed over the years. It was observed that network effects—that is, interactions and energized responses that influenced the dynamics of the entire network—had to be taken into account in order to examine these mechanisms.

Early research raised fundamental concerns of this kind, which serve as the basis for current initiatives to comprehend intricate reaction networks.

Nowadays, one of the most important components of theoretical chemical kinetics is computation. It is important to remember that the direct simulation of global models using fundamental physical equations, like Newton's equations of motion, has been presented recently. Global simulations allow researchers to capture full systems, in contrast to most systems that restrict realities to mechanical sequential operations. Although this eliminates the requirement for rudimentary physical representations, it causes issues with the time and size scales that are typical in real-world systems. For example, there are difficulties in accurately translating the sub-femtosecond motions of atoms and the microseconds to years that characterize many chemical processes in molecular dynamics simulations. Due to this constraint, multiscale simulation techniques that can manage such disparate scales have been refined.

The master equation, which is a mathematical description of how a population of certain states evolves if specific types of transitions between these states are feasible, is another essential component of modern kinetics. Master equations provide a model for the likelihood of state transitions by assuming the Markov property, which states that the future state depends exclusively on the present. The master equation finds wide-ranging use since these states may correspond to chemical species, vibrational-rotational states, or some specific molecular orientation. More detailed substates and intricate numerical calculations are necessary because some issues arise in non-Markovian systems or systems that never come close to an internal equilibrium. Even if theoretical frameworks and computing have advanced, there are still issues with complex system research. For instance, because they traverse across several PES valleys, synchronous transition processes, such as conformation or transition state ensembles, can be very challenging to explain clearly. Furthermore, because raw outputs may include large and intricate matrices, comprehending the nuances of geophysical models necessitates novel techniques to data interpretation. The current work focuses on recent developments in kinetic modelling applied to complicated systems with these concerns in mind. Instead of offering a comprehensive overview of the article, it aims to concentrate on a few themes, including network effects, navigating the complexity of reaction mechanisms, and computational and theoretical synergy. By tackling these problems, the current viewpoint seeks to advance our understanding of reaction dynamics and provide a basis for future advancement in this still-emerging field of study.

Insights into Reaction Dynamics and Mechanistic Pathways

Important tools for increasing the precision of chemical processes that are challenging to investigate only through experimental means were made available by theoretical kinetics. These include interstellar chemistry, atmospheric chemistry, and high temperature combustion systems. The master equation, which is the collection of combined rate equations for a complete series of stages in the reaction mechanism, is the most exacting method to use when building such systems. The rate constants of such mechanisms are frequently determined in the classical and state-selective Transition State Theory (TST).

Transition State Theory (TST)

Thus, a mathematical approach to determining rate constants in connection to molecule energy profiles is provided by time series analysis, or TST. The assessment of the thermal rate coefficient at the specified temperature TTT is the basis of TST:

$$k(T) = \kappa \frac{k_B T}{h} \frac{Q^\ddagger}{Q_R} e^{-\frac{V^\ddagger}{RT}}$$

Where:

- V^\ddagger : Energy barrier at the transition state.
- Q^\ddagger : Partition function for the transition state.
- Q_R : Partition function for reactants.
- κ : Transmission coefficient accounting for quantum tunneling and recrossing corrections.
- k_B and h : Boltzmann and Planck constants, respectively.

Conventional TST evaluates V^\ddagger and Q^\ddagger at the saddle point on the potential energy surface (PES), while **Variational TST** refines this by considering the maximum free energy along the reaction path, minimizing recrossing and increasing the accuracy of κ .

Advances in Computational Approaches

1. Electronic Structure Calculations: Ab initio techniques like density functional theory (DFT) and coupled cluster theory (CCSD(T)) were used to predict PES features like barrier heights and reaction energies in the past. These techniques can also provide an accurate mechanistic representation of the polyatomic systems and solve difficulties starting with diatomic molecules.

2. Tunnelling and Quantum Effects: Advanced TSTs have quantum characteristics, such as tunnelling and zero point oscillations, and are employed semiquantitatively, as in WKB. These adjustments are a component of IC(α SF) and are especially pertinent to actual rate computations at low temperatures.

3. Master Equation Modelling: The master equation formalism connects internal energy transfers between molecular states and macroscopic variables to the microcanonical rate constants resulting from TST. When dealing with intermediates, radical species, and nonequilibrium systems, the stepped pressure-jump technique is very crucial.

4. Partition functions and entropy: Quantifying entropic observations of reaction rates requires a thorough understanding of partition functions, anharmonic effects, and mode-coupling effects. Such difficulties regarding the TS are taken into consideration by the variable reaction coordinate (VRC)-TST, which is pertinent to barrierless processes.

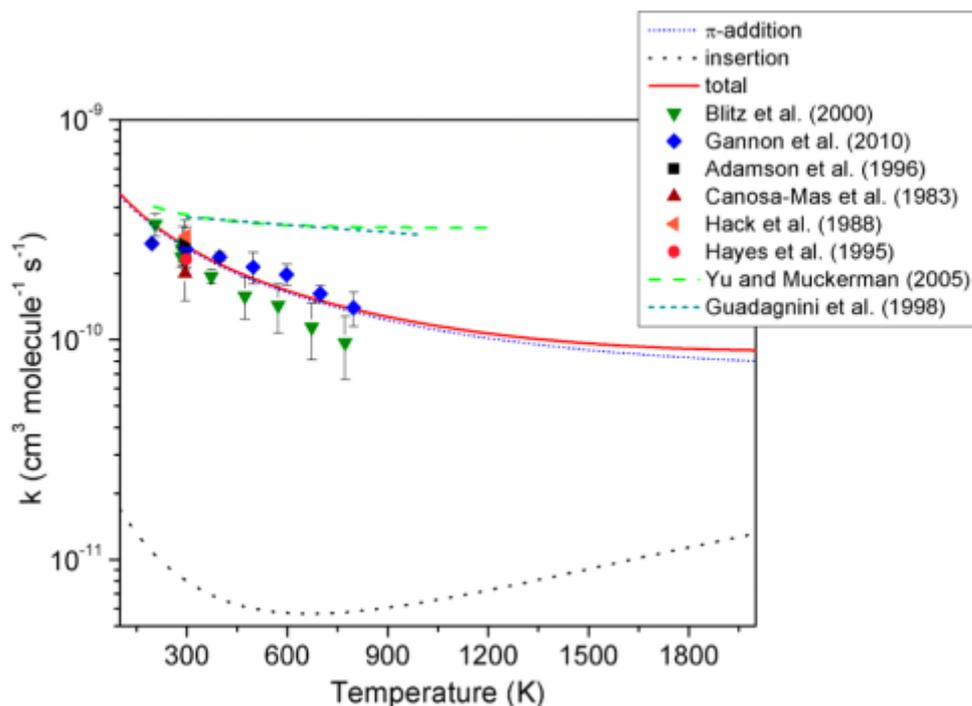


Figure 1: **Temperature Dependence of Reaction Rate Constants: Insights from Transition State Theory and Theoretical Kinetics**

The development of chemical reaction mechanisms, including those that are challenging to investigate empirically, such as modern combustion, atmospheric chemistry, and interstellar chemistry, depends heavily on theoretical kinetics. Nonetheless, a framework that is widely utilized in this context is the master equation, which offers the coupled rate equations for each step in a network's reaction mechanism. The standard and optimal rate constants that are pertinent to the Transition State Theory (TST) are frequently used in these equations. With evaluation of the energy barrier and the molecular properties in the transition state over the reaction coordinate, TST offers a very straightforward way to approximate the total potential for a reaction to occur.

Such predictions are now even more accurate because to recent developments in computational chemistry. PES and other features like reaction energies and barriers can be constructed using precise techniques like density functional theory (DFT) and coupled cluster (CCSDT(Q)) at the electronic structure level. By discounting the mistakes caused by quantum mechanical tunnelling and TS crossover, variational TST increases the predictions. This is particularly crucial when there is a low temperature or when there are several interconnected parts and subsystems because energy is transferred between molecular states in accordance with quantum mechanics. In order to estimate rates in reactions with

a small barrier, such as radical recombination, modern approaches also require a high level of description of entropic effects and high-order anharmonicity. Applications ranging from atmospheric and astrochemical reactions to combustion chemistry have made extensive use of these instruments, which offer valuable information on product speciation and reaction processes. Large molecular networks and multireference systems simulation still have certain issues, however advances in SCM techniques are gradually closing the gap between theoretical and experimental evidence.

Molecular and Atomic Processes controlling Chemical Reactions at Solid and Gas Phase Interfaces as well as in Liquid Media and in Enzymes

When it comes to the types of systems involved and their sizes, molecular phase reactions differ from gas phase reactions. More significantly, the actual condensed phases are not as complex as the current image suggests. For example, the crystal-air interface interactions involve defects, reconstruction, and relaxation, which are further complicated by surface coverage.

Solid-Gas Interfaces

This is a problem since precious metals like Pt and Pd can oxidize NO in car exhaust systems. Rate constants for adsorption, dissociation, or reaction may be present in simple models, but they do not take into consideration factors like surface coverage or the associated changes in atomic sites, binding energies, and rates. For instance, Pt(111) exhibits an increase in oxygen binding energy from 4.39 eV at low coverages to 4.49 eV at large coverages. In particular, surface coverage and lateral contacts have a significant impact on the reaction's driving force, which causes it to change thermodynamically from being almost isenthalpic to being somewhat exothermic as coverage increases.

To choose the best exchange correlation potential, the following problems must be fixed: To understand the lateral interaction, huge super cell simulations have been conducted to integrate such effects. There are further challenges with thermodynamics' configurational and vibrational entropy. One of the kinetic modelling tools used in this work is the mean-field kinetic Monte Carlo, which simulates the interactions at the surface by averaging the rate constants over coverages. A more comprehensive approach involves simulating individual site occupancies under reaction conditions and reaction pathways; however, this is impractical for large or disordered materials due to the large number of reaction processes.

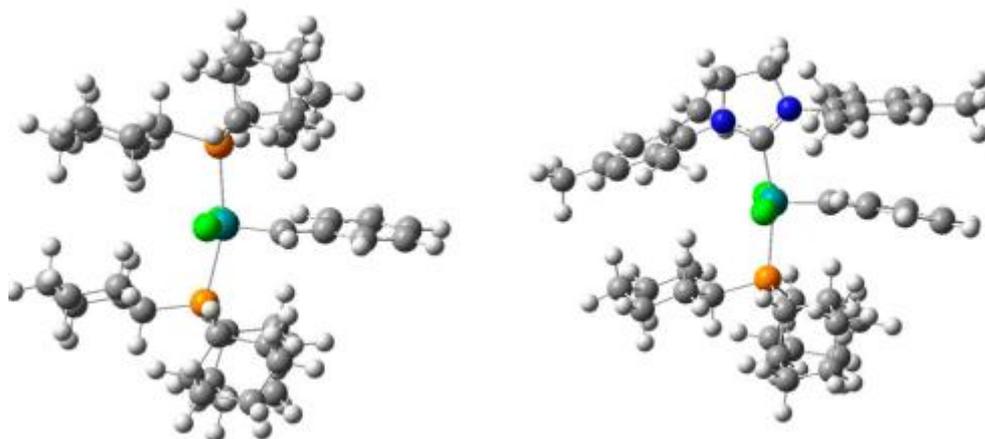
The connection between fluid dynamics and molecular reaction kinetics presents additional challenges, including issues with heterogeneous catalysis and gas-phase combustion. In order to solve real-world energy and environmental issues, simulation is done at both the molecular and macroscopic scales in a process known as mesoscale modelling. Additionally, researchers must decide between cluster models, which are more suitable for nonperiodic sites but also computationally expensive, and periodic models, which are helpful for ordered crystal lattices.

Nevertheless, advancements have been made, as demonstrated by early point chemistry procedures like H₂ dissociative chemisorption on metal surfaces associated with the Haber-Bosch synthesis. To fine-tune the rate estimates, these efforts rely on precise quantum mechanical methods and molecular beam observations, with a focus on reactions occurring on clearly defined metal facets like terraces or steps.

Reactions in Solution

As can be demonstrated, compared to gas-solid interfaces, liquid-phase processes present both benefits and challenges. Even though fluids are arguably random, they typically allow for the homogeneity assumption. Statistical mechanical averaging over ensembles is necessary to define rates for reactions in solutions, and using the entire system of high level electronic structure considerations makes this process quite costly. By focusing on computational computations on the reactive subsystem and simulating the wider environment, fragment or QM/MM techniques address this difficulty. Then, without showing solvent molecules in a medium, continuum solvation models characterize solvents as dielectrics that take into account electrostatic and solvation effects. These techniques are appropriate for the investigation of solution-phase reactions because they strike a balance between accuracy and computer computability.

For example, contemporary methods have been used to explain patterns like Diels-Alder reactions, solvent variation on hydrogen radical staunchness, and free radical abeyance. These works demonstrate how theoretical approaches can be used to identify chemical processes in complicated systems. The field is now able to analyze the kinetics and dynamic aspects of chemical processes at gas/solid and liquid phase systems as well as enzyme milieu thanks to further advancements in computational methodology and theoretical advancements. These are more crucial for solving real-world issues than industrial chemistry, energy, and the environment.



In order to visualize molecular shapes and atom-to-atom bonds, the graphic displays two molecular structures using the ball and stick metaphor, which is common in chemistry. Each sphere represents an atom, and different colours represent different elements: orange typically represents oxygen, green may represent heavier atoms like sulphur or chlorine, blue represents nitrogen, and grey typically represents carbon. Covalent bonds are indicated by the line connecting the spheres; single covalent bonds are indicated by dotted lines, while double or triple covalent bonds are indicated by two or three dots, respectively. In order to demonstrate direction, which is essential in chemical and biological processes, some of the models are placed in three dimensions. The atoms' relative orientation points to conformational flexibility, which is a key component of the molecules' stability, reactivity, and interactions. These traits may reveal their role in a particular context, such as distinct pharmacological activities or routes. More details about them or a larger context in which to discuss them would be beneficial.

FINDINGS

One of the fundamental theories of chemical kinetics is called transition state theory, or TST. Its goal is to estimate specific reaction rates by estimating energy barriers and other transition state parameters. In addition to zero-point energies, which stand for the ground-level quantum-mechanical energy, TST effectively accounts for electron tunnelling, which is a particle passing through barriers of potential energy. Since these characteristics enable the fine details of molecular motion and energy distributions, which are crucial at low temperatures and in complicated systems, they are particularly helpful for figuring out the proper reaction rates in temperature-dependent systems. The theories explaining chemical kinetics are now much more accurate and applicable thanks to recent advances in computational chemistry. For precise PES calculations, quantum computing is intimately tied to a number of high-level electronic structure techniques, including the density functional theory (DFT) and the coupled cluster approach, such as the CCSD(T). Because they provide a clear plot of energy along a reaction coordinate, these surfaces are highly helpful in illustrating the reaction mechanism. Similarly, multiscale modelling takes into account behaviours in systems with different temporal and spatial dimensions, such as catalysis processes or instances of enzyme catalysis, by combining quantum calculations and molecular dynamics.

Complex systems are still difficult to comprehend, though. This category includes mechanisms that identify several stages, various intermediates, or reactions occurring in disordered media, such as amorphous solids and heterogeneous surfaces. These systems are typically difficult to model because of the interdependencies across several processes and the intricacy of energy profiles. Only new computational approaches and a deeper comprehension of how molecular interactions vary across time and place will be able to overcome these obstacles. These advancements have many important applications in almost every sector, from manufacturing to environmental protection. The use of theoretical models in combustion chemistry aids in fuel selection and emission reduction. Furthermore, advanced kinetics techniques are used to study atmospheric reactions that are crucial to the study of pollution and climate change. These instruments are also necessary for studying interstellar chemistry in order to comprehend the processes that govern molecular formation under extreme circumstances. In a variety of industries, including medicines and energy, precise projected reaction rates and mechanistic insights are helpful for developing reaction enhancements. These illustrations highlight the need for theoretical and computational developments in relation to the real-world problems facing the scientific and engineering disciplines.

CONCLUSION

Through theoretical and computational approaches that provide highly effective applications for quantitatively evaluating and forecasting chemical reactions, chemical kinetics has undergone an incredibly enlightening revolution. By specifying the energy maximum that molecules must cross throughout a chemical shift, Transition State Theory, or

TST, continues to serve as a theory that contributes to our understanding of reaction rates. TST gives the researcher comprehensive reaction paths that were previously unattainable when combined with quantum mechanical studies of tunnelling and zero-point energy. These techniques are crucial for researching complex gas-phase processes, biological and technological systems, and the thermodynamics of reactions, selectivity, and mechanisms in reactions that take place under temperature influences.

Computational methods such as multiscale simulations and high level electrical structure have been essential to these developments. These tools aid in the atomic-level description of potential energy surfaces (PES), or the energies along reaction coordinates necessary for precise rate estimates. Similar to this, scientists can now study and quantify atomic and macroscopic system level scales—such as enzyme catalysis, heterogeneous interfaces, and liquid-phase reactions—through computer simulations thanks to the availability of multiscale simulation methods. A more precise picture of the reactions is produced by these advancements, which allow the scientists to address issues in time scales and spatial regions that are entirely different from one another.

However, several obstacles to integration still exist. Existing theoretical frameworks and computational tools continue to struggle with systems that have numerous process steps, a large number of intermediates, or disorder, such as amorphous solids and heterogeneous catalysts. Even the biggest and most potent computers are still unable to accurately simulate such systems, and new frameworks need to account for network effects, out-of-equilibrium behaviour, and the random processes that are a part of chemical reactions. Furthermore, there are significant conceptual and technological obstacles when applying these techniques to investigate the kinetics and dynamics of both micro and macro reactions in various reaction environment compartments, such as gas-solid interfaces, liquid solution media, and biological systems. The ongoing development in chemical kinetics has important practical ramifications in addition to being a scientific endeavour. At the molecular level, supplements such as combustion reactions in energy generation can point the way toward cleaner and more effective fuel use. Gaseous reaction kinetic models help produce scientific information about the climate and air quality that is pertinent to the environment. These discoveries aid in the design of sustainable processes and the balancing of reaction conditions in industrial chemistry, particularly in catalysis. As a result, the combination of theoretical and computational methods continues to be the most effective way to solve global issues, generate new knowledge, and define the direction of science and technology.

REFERENCES

- [1]. Baer, T., & Hase, W. L. (1996). *Unimolecular Reaction Dynamics: Theory and Experiments*. Oxford University Press.
- [2]. Benson, S. W. (1968). *Thermochemical Kinetics*. Wiley.
- [3]. Bixon, M., & Jortner, J. (1999). Electron transfer—from isolated molecules to biomolecules. *Advances in Chemical Physics*, 106, 35–202. <https://doi.org/10.1002/9780470141731.ch2>
- [4]. Carpenter, B. K. (2005). *Determination of Organic Reaction Mechanisms*. Wiley-Interscience.
- [5]. Chang, R. (2016). *Physical Chemistry for the Biosciences*. University Science Books.
- [6]. Crim, F. F. (2008). Chemical dynamics of molecules in excited electronic states. *Journal of Physical Chemistry A*, 112(41), 9481–9488. <https://doi.org/10.1021/jp806249b>
- [7]. Eyring, H. (1935). The activated complex in chemical reactions. *Journal of Chemical Physics*, 3(2), 107–115. <https://doi.org/10.1063/1.1749604>
- [8]. Fleming, G. R., & Scholes, G. D. (2004). Quantum mechanics for reaction dynamics. *Nature*, 431(7012), 256–261. <https://doi.org/10.1038/nature02871>
- [9]. Frenklach, M., & Wang, H. (1994). Detailed modeling of soot particle nucleation and growth. *Proceedings of the Combustion Institute*, 23(1), 1559–1566. [https://doi.org/10.1016/S0082-0784\(06\)80426-1](https://doi.org/10.1016/S0082-0784(06)80426-1)
- [10]. Gao, J., Truhlar, D. G., & Cramer, C. J. (1998). Quantum mechanical methods for modeling enzymatic reactions. *Accounts of Chemical Research*, 31(8), 559–566. <https://doi.org/10.1021/ar970001q>
- [11]. Hammes-Schiffer, S., & Soudackov, A. V. (2008). Proton-coupled electron transfer in solution, proteins, and electrochemistry. *Journal of the American Chemical Society*, 130(48), 15334–15342. <https://doi.org/10.1021/ja805537p>
- [12]. Hess, B., & Haider, K. (2002). Molecular dynamics simulations of biomolecules: Long-term simulations and essential dynamics. *Biophysical Chemistry*, 101–102, 255–267. [https://doi.org/10.1016/S0301-4622\(02\)00029-2](https://doi.org/10.1016/S0301-4622(02)00029-2)
- [13]. Johnston, H. S. (1966). *Gas Phase Reaction Rate Theory*. Ronald Press Company.
- [14]. Karplus, M. (2000). Aspects of protein reaction dynamics: Deviations from simple behavior. *Journal of Physical Chemistry B*, 104(1), 11–27. <https://doi.org/10.1021/jp993716l>
- [15]. Levine, R. D. (2009). *Molecular Reaction Dynamics*. Cambridge University Press.
- [16]. Lin, H., & Truhlar, D. G. (2007). QM/MM: What have we learned, where are we, and where do we go from here? *Theoretical Chemistry Accounts*, 117, 185–199. <https://doi.org/10.1007/s00214-006-0143-z>
- [17]. Lindemann, F. A. (1922). Discussion on the radiation formula of the gas reaction velocity. *Transactions of the Faraday Society*, 17, 598–606. <https://doi.org/10.1039/TF9221700598>
- [18]. Marcus, R. A. (1993). Electron transfer reactions in chemistry: Theory and experiment. *Reviews of Modern Physics*, 65(3), 599–610. <https://doi.org/10.1103/RevModPhys.65.599>

- [19]. Mikkelsen, K. V., & Ratner, M. A. (1988). Electron transfer in condensed phases. *Chemical Reviews*, 88(1), 97–131. <https://doi.org/10.1021/cr00083a005>
- [20]. Milestane, A., & Bryantsev, V. (2011). Nonadiabatic reactions and solvent effects. *Journal of Chemical Theory and Computation*, 7(12), 3969–3978. <https://doi.org/10.1021/ct200590a>
- [21]. Paul, H. W. (2000). *Dynamics of Molecular Collisions*. Springer.
- [22]. Pople, J. A., & Hehre, W. J. (1972). Approximate molecular orbital theory. *Journal of Chemical Physics*, 56(5), 2685–2689. <https://doi.org/10.1063/1.1677527>
- [23]. Raff, L. M., & Komanduri, R. (2012). *Principles of Molecular Reaction Dynamics*. Springer.
- [24]. Rice, O. K., Ramsperger, H. C., & Kassel, L. S. (1927). Theories of unimolecular reactions. *Journal of the American Chemical Society*, 49(7), 1617–1626. <https://doi.org/10.1021/ja01407a001>
- [25]. Schwartz, B. J., & Alavi, A. (2001). Time-dependent quantum mechanics of chemical reactions. *Chemical Physics Letters*, 343(3–4), 399–408. [https://doi.org/10.1016/S0009-2614\(01\)00669-5](https://doi.org/10.1016/S0009-2614(01)00669-5)
- [26]. Smith, I. W. M. (1980). *Kinetics and Dynamics of Elementary Gas Reactions*. Butterworths.
- [27]. Truhlar, D. G., & Garrett, B. C. (1984). Variational transition state theory. *Annual Review of Physical Chemistry*, 35(1), 159–189. <https://doi.org/10.1146/annurev.pc.35.100184.001111>
- [28]. Tully, J. C. (1990). Molecular dynamics with electronic transitions. *Journal of Chemical Physics*, 93(2), 1061–1071. <https://doi.org/10.1063/1.459170>
- [29]. Turro, N. J., Ramamurthy, V., & Scaiano, J. C. (2010). *Principles of Molecular Photochemistry: An Introduction*. University Science Books.
- [30]. Warshel, A., & Levitt, M. (1976). Theoretical studies of enzymatic reactions: Dielectric, electrostatic, and steric stabilization of the carbonium ion in the reaction of lysozyme. *Journal of Molecular Biology*, 103(2), 227–249. [https://doi.org/10.1016/0022-2836\(76\)90311-9](https://doi.org/10.1016/0022-2836(76)90311-9)
- [31]. Weiss, J. (1935). A theory of activation and reaction velocity. *Nature*, 136(3438), 1014–1015. <https://doi.org/10.1038/1361014a0>
- [32]. Wilson, S. (1981). *Electron Correlation in Molecules*. Clarendon Press.
- [33]. Wong, M. W. (2016). Solvation and solvent effects in computational chemistry. *Reviews in Computational Chemistry*, 29, 141–162. <https://doi.org/10.1002/9781119282580.ch4>
- [34]. Woodward, R. B., & Hoffmann, R. (1970). The conservation of orbital symmetry. *Angewandte Chemie International Edition*, 8(11), 781–853. <https://doi.org/10.1002/anie.197007811>
- [35]. Wigner, E. (1938). The transition state in chemical reactions. *Transactions of the Faraday Society*, 34, 29–41. <https://doi.org/10.1039/TF9383400029>