From Marcus to Iteration: Recasting Electron Transfer as Discrete Configuration Sampling

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Electron transfer reactions underpin essential processes in chemistry, biology, and materials science. Rudolph A. Marcus' groundbreaking theory explained these reactions through the interplay of thermodynamic driving force and reorganization energy, leading to a rate expression that accurately predicts both "normal" and "inverted" behavior. While Marcus theory is traditionally framed in continuous time, it fundamentally relies on the probabilistic sampling of nuclear configurations, where an electron transfer occurs only when the donor and acceptor energy surfaces align. In this paper, we make that sampling process explicit by recasting electron transfer as a series of discrete iterations. Each iteration represents an attempt to reach the configuration required for charge transfer, with success probability governed by Boltzmann-weighted energetic overlap. This iteration-based framework allows us to derive the Marcus rate expression from first principles, reinterpreting the rate constant as the product of attempt frequency and per-iteration success probability. In doing so, we connect classical rate theory to a discrete, causal view of molecular dynamics and open new possibilities for modeling biological electron transfer as a form of logical computation.

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1. Introduction

Electron transfer reactions lie at the heart of redox chemistry, energy transduction, and molecular electronics. In biological systems, they drive the photosynthetic and respiratory chains, enabling efficient charge movement across protein complexes. In synthetic systems, they underlie the function of solar cells, batteries, and catalytic cycles. A quantitative understanding of these reactions is therefore essential across disciplines. The foundational framework for describing such reactions was developed by Rudolph A. Marcus in the mid-20th century. His theory offered a revolutionary insight: the rate of electron transfer is determined not merely by the thermodynamic driving force but also by the energy required to reorganize the molecular environment during the transition. This reorganization energy defines the curvature and overlap of potential energy surfaces between donor and acceptor states.

1.1 Overview of Marcus Electron Transfer Theory

Marcus theory models the electron transfer process as a nonadiabatic transition between electronic states, each embedded within a parabolic potential energy surface corresponding to different nuclear configurations. These surfaces represent the reactant and product states, and their intersection defines the energetic condition under which electron transfer becomes most favorable. The probability of transfer depends on how frequently the nuclear coordinates fluctuate into configurations where these surfaces align closely enough for the electron to tunnel across. The resulting rate expression, often written as:

$$k_{\mathrm{ET}} = A \cdot \exp\left[-\frac{(\Delta G^{\circ} + \lambda)^2}{4\lambda k_B T}\right],$$

accounts for both the thermodynamic driving force ΔG∘ and the reorganization energy λ. This model predicts the famous “inverted region,” where excessive driving force slows the reaction—a counterintuitive yet experimentally verified outcome. Marcus’ formulation transformed our understanding of redox chemistry by grounding electron transfer in statistical thermodynamics and quantum mechanics.

1.2 Limitations of the Continuous-Time Paradigm

Despite its success, the traditional presentation of Marcus theory is embedded in a continuous-time formalism. Time appears explicitly or implicitly in the use of rate constants, differential equations, and relaxation dynamics. However, in molecular systems—especially in biological or nanoscopic contexts—time may not be the most natural or meaningful variable. At these scales, processes occur in discrete steps: molecules fluctuate between configurations, interactions happen stochastically, and events such as electron transfers occur in response to well-defined energetic conditions rather than progressing through uniform temporal flows. The assumption of smooth time evolution obscures the causal structure of the underlying events. Moreover, it masks the role of logical gating and conditional readiness, which are increasingly important in interpreting complex systems such as reaction centers, enzyme networks, and synthetic molecular circuits.

1.3 Motivation for an Iteration-Based Reinterpretation

We propose an alternative view: to treat electron transfer not as a time-evolved process but as a series of discrete iterations—attempts made by a fluctuating system to reach the configuration required for charge transfer. Each iteration represents a sample of the reaction coordinate space, thermally driven and causally isolated. Electron transfer occurs when an iteration coincides with the energetic alignment necessary for tunneling. In this framework, the traditional rate constant becomes the product of two factors: the attempt frequency (i.e., the average number of configuration samples per unit time) and the probability of success per attempt, which we show is equivalent to the Marcus exponential term. By making iteration explicit, we recover Marcus theory as an emergent result and recast electron transfer as a logic-driven, event-based process. This shift aligns with both computational modeling approaches and experimental realities in systems where time is difficult to define or measure directly. It also opens the door to reinterpreting biochemical reactions—including photosynthetic charge separation and redox logic in enzymes—as fundamentally informational processes.

2. Foundations of Iteration-Based Modeling

The notion of iteration-based modeling originates in a desire to describe physical processes not in terms of a continuously flowing time variable, but rather as a sequence of discrete, causally linked attempts to advance a system from one state to another. In the context of electron transfer, this means describing the reaction as a stepwise process in which each step—or iteration—corresponds to a trial configuration of the donor–acceptor system, driven by internal fluctuations. By framing dynamics in terms of discrete sampling rather than time, we aim to recover classical results such as Marcus theory from first principles while revealing new insights into the underlying logic of molecular change.

2.1 Defining Iterations as Discrete Configuration Sampling Steps

In the iteration-based framework, we define an iteration as a single event in which the nuclear coordinates of the donor–acceptor system sample a thermally accessible configuration. This may be due to internal molecular vibrations, solvent dynamics, or collective protein motions in biological environments. Each iteration represents a distinct sample of the reaction coordinate qqq, and can be understood as a stochastic probe of whether the energetic alignment needed for electron transfer has been achieved. Iterations are not uniform in time; they are conceptually distinct from clocked events. They are causal updates, akin to frames in a computation or steps in a stochastic process, each with the potential to trigger an outcome—namely, electron transfer—if the conditions are met.

In this model, the reaction coordinate landscape is not a smooth trajectory but a high-dimensional surface explored point-by-point. This aligns with modern views in molecular dynamics and statistical mechanics, where reaction progress is often understood in terms of discrete transitions between metastable states.

2.2 Relation to Thermal Fluctuations and Solvent Reorganization

Marcus theory emphasizes the critical role of reorganization energy λ, the energetic cost of shifting the molecular and solvent environment to accommodate the electronic change. In traditional time-based models, these fluctuations are implicit in the temperature-dependent terms and activation barriers. In the

iteration-based approach, we make these fluctuations explicit: each iteration represents one thermally driven rearrangement of the surrounding environment, such that the relative energies of the donor and acceptor shift.

The Gaussian distribution of nuclear configurations that underlies Marcus theory corresponds here to the probability density over iterations. The solvent and intramolecular environment are constantly sampling configurations drawn from this distribution. When the sampled configuration brings the system to the point where donor and acceptor energy levels align, electron transfer becomes possible.

Thus, solvent reorganization and thermal motion are not continuous relaxations, but discrete sampling events, each potentially providing the proper conditions for the reaction to proceed. Time as a parameter becomes a function of the frequency of sampling, not a direct measure of reaction progress.

2.3 The Concept of Per-Iteration Success Probability

At the heart of the iteration-based model is the per-iteration success probability, denoted P_succ. This is the probability that a single configuration sampling event leads to successful electron transfer. It captures the likelihood that an iteration results in a nuclear geometry at which the electronic energy levels of the donor and acceptor align sufficiently for a tunneling event to occur.

Mathematically, P_succ corresponds to the Boltzmann-weighted overlap of the donor and acceptor energy surfaces. In Marcus theory, the exponential term in the rate expression reflects the probability of such an alignment, integrated over the configuration space. In the iteration framework, this term arises naturally as the probability of success per discrete sampling attempt:

$$P_{\text{succ}} = \exp\left[-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_B T}\right].$$

This probability is independent of the number of attempts—it is a property of the system's energy landscape and thermal fluctuations. The observed rate constant is then the product of this intrinsic success probability and the attempt frequency, which depends on how often these sampling events occur. This shifts the

conceptual weight from time as a continuous background to event-driven causality, where time emerges only as an average spacing between meaningful iterations.

3. Classical Marcus Theory Revisited

Marcus theory, first introduced by Rudolph A. Marcus in the 1950s and later extended in the 1960s, provided the first comprehensive quantum-statistical treatment of electron transfer (ET) reactions in condensed phase systems. It remains one of the most elegant and predictive models in physical chemistry, with applications spanning organic redox reactions, inorganic coordination complexes, electrochemistry, and biological electron transfer chains such as those found in photosynthesis and respiration. At its core, Marcus theory accounts for how the nuclear environment (molecular geometry, solvent polarization, vibrational modes) must reorganize to enable charge transfer between donor and acceptor species. It formalized the probabilistic nature of electron transfer as a nonadiabatic transition, driven by quantum tunneling and modulated by classical thermal fluctuations.

3.1 The Original Formulation and Exponential Rate Expression

Marcus derived the rate of electron transfer from Fermi's Golden Rule, incorporating a Franck–Condon-like approach to nuclear configuration overlap. In his original treatment, he modeled the donor and acceptor states as harmonic potential energy surfaces (parabolas) displaced along a collective reaction coordinate qqq, which encompasses both molecular and solvent degrees of freedom.

The classical Marcus rate expression is given by:

$$k_{\mathrm{ET}} = A \cdot \exp\left[-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_B T}\right],$$

where:

- k_{ET} is the rate of electron transfer,
- A is a pre-exponential factor related to electronic coupling and nuclear vibrational frequencies,
- ΔG° is the standard free energy change of the reaction,
- λ is the reorganization energy,
- k_B is Boltzmann's constant,
- T is the absolute temperature.

This expression yields a **Gaussian dependence** of the transfer rate on the thermodynamic driving force ΔG°, peaking when $\Delta G^\circ = -\lambda$, and giving rise to the now-famous **Marcus inverted region**, where increasing exergonicity actually decreases the transfer rate.

3.2 Energetic Alignment and the Crossing Point

The central insight of Marcus theory is that electron transfer is only probable when the total energy of the reactant state equals that of the product state for a given nuclear configuration. In the parabolic potential model, this condition corresponds to the intersection point of the donor and acceptor energy surfaces. Importantly, because the nuclear environment fluctuates due to thermal motion, the system continually samples different configurations of the reaction coordinate.

Electron transfer becomes possible when such a configuration coincides with the crossing point, i.e., when the energies of the initial and final electronic states are degenerate. The probability of the system reaching this configuration is governed by the Boltzmann distribution of nuclear configurations in the reactant state. The rate of transfer is then proportional to the likelihood of reaching this crossing point, modulated by the tunneling probability and the strength of electronic coupling.

In this framework, energetic alignment is not achieved by deterministic motion toward the crossing point but by thermal sampling—a stochastic process

governed by fluctuations in molecular and solvent coordinates. This probabilistic interpretation is precisely what makes Marcus theory amenable to reinterpretation in iteration space.

3.3 Role of Reorganization Energy in Activation

The reorganization energy λ quantifies the amount of energy required to reorganize the nuclear configuration of the system—both intramolecular and solvent—so that electron transfer becomes thermodynamically feasible. It is defined as the energy cost of shifting the nuclear coordinates of the reactant to those of the product *without* transferring the electron.

In the Marcus model, λ determines the curvature and horizontal displacement of the parabolic potential energy surfaces, thereby influencing both the **position of the crossing point** and the **height of the activation barrier**. For small driving forces $|\Delta G^\circ| \ll \lambda$, the activation energy is roughly linear in ΔG°, consistent with Arrhenius behavior. However, as ΔG° becomes more negative, the barrier initially decreases, reaching a minimum at $\Delta G^\circ = -\lambda$, after which it increases again—this leads to the inverted region.

In this model, activation arises not from a fixed energy barrier but from the need to borrow thermal energy to distort the environment to the right configuration. Reorganization energy thus serves as a measure of how demanding the environment is in facilitating electron transfer. From an iteration perspective, it corresponds to how unlikely it is that any given configuration sampling (iteration) will succeed. Larger λ values imply that a rarer fluctuation is needed to achieve alignment, reducing the success probability per iteration.

By reframing λ in terms of statistical sampling difficulty, we prepare the ground for its reinterpretation as a gating parameter in an iteration-based model, where reaction time is not a continuous background but the outcome of cumulative probabilistic attempts.

4. Deriving Marcus from Discrete Sampling

In this section, we reconstruct the classical Marcus rate expression from the ground up using an iteration-based framework. The key premise is that the donor–acceptor system does not evolve continuously in time, but rather explores

its nuclear configuration space through a sequence of discrete sampling events—iterations. Each iteration corresponds to a thermally driven fluctuation in the reaction coordinate, and electron transfer occurs only when the system's configuration meets a specific alignment condition. This discrete, stochastic view makes explicit the logic that underlies the probabilistic core of Marcus theory and demonstrates how the exponential term in the rate constant emerges naturally from statistical sampling.

4.1 Iteration as Configuration Sampling

Let us define an iteration as a single, physically meaningful sample of the system's nuclear configuration qqq. These configurations are drawn from a Boltzmann-distributed ensemble representing thermal equilibrium. In each iteration, the system probes a different geometry, driven by solvent motion, bond stretching, torsional vibrations, or protein breathing modes. These fluctuations do not progress linearly along a reaction coordinate but rather represent multidimensional excursions in the potential energy landscape.

The total probability of electron transfer over a large number of such iterations depends on the probability that one of these configurations meets the condition for tunneling—namely, when the energies of the initial and final electronic states are degenerate at that geometry. Electron transfer is then viewed as a logical gate embedded in a stochastic sampling process: an event that occurs only when the sampled state meets strict energetic conditions.

4.2 Gaussian Statistics of Fluctuation Around Equilibrium

In Marcus theory, the energy surfaces of the reactant and product states are modeled as harmonic potentials—parabolas—centered at different nuclear configurations. Thermal fluctuations of the system cause the nuclear configuration to explore these surfaces, resulting in a probability distribution over possible qqq values. For a harmonic oscillator near equilibrium, this distribution is approximately Gaussian:

$$\rho(q) \propto \exp\left(-\frac{(q-q_0)^2}{2\sigma^2}\right),$$

where q_0 is the equilibrium configuration of the initial state, and σ characterizes the thermal width of the distribution. The reaction coordinate q thus samples values around q_0, and the likelihood of reaching the critical value $q^\ddagger$ (the point of energy degeneracy) is governed by this Gaussian envelope.

These statistics are central to Marcus theory, though traditionally expressed in continuous terms. In the iteration framework, they define the per-iteration sampling probability density. That is, every iteration probabilistically draws a value of q from this distribution.

4.3 Success Criterion: Alignment at Crossing Point

Electron transfer becomes feasible when the nuclear configuration q causes the energies of the donor and acceptor electronic states to become equal. For parabolic energy surfaces, this condition defines the crossing point, denoted q‡. The probability of successful electron transfer in any iteration is thus equivalent to the probability of sampling q≈q‡ within the Gaussian ensemble of nuclear fluctuations.

Since this is a narrow region of the overall configuration space, most iterations will not satisfy the alignment condition and thus will not lead to electron transfer. The success rate per iteration, P_succ, is the fraction of iterations in which the system samples a configuration sufficiently close to q‡ for the transition to occur. This probability is what ultimately governs the exponential term in the rate constant.

Mathematically, this is expressed as:

$$P_{\text{succ}} \propto \rho(q^\ddagger) \propto \exp\left(-\frac{(q^\ddagger-q_0)^2}{2\sigma^2}\right).$$

This expression quantifies the rarity of the crossing-point configuration within the thermally accessible ensemble of nuclear states.

4.4 Derivation of the Exponential Term from Per-Iteration Probability

To connect this to the classical Marcus rate expression, we now relate the Gaussian statistics of nuclear sampling to the energy parameters of electron transfer. The energy difference between the minimum of the reactant state and the crossing point q‡ is the activation energy, given by Marcus as:

$$\Delta G^{\ddagger} = \frac{(\Delta G^{\circ} + \lambda)^2}{4\lambda}.$$

This activation energy reflects the amount of thermal energy required to bring the system from its equilibrium configuration to the configuration where donor and acceptor energies are equal.

Now, because the system samples configurations with Boltzmann-weighted probabilities, the probability of reaching q‡ in any single iteration is:

$$k_{\mathrm{ET}} = \frac{1}{\tau_{\mathrm{iter}}} \cdot P_{\mathrm{succ}},$$

where:

- τ_{iter} is the average time between configuration sampling events (i.e., the inverse of the attempt frequency),
- P_{succ} is the success probability per iteration.

Thus, the Marcus rate emerges as the product of an intrinsic sampling frequency and a logical success criterion, entirely in line with the discrete iteration framework. Time is no longer a continuous backdrop but an emergent consequence of the rate at which configuration sampling—and thus potential reaction events—occur.

This derivation confirms that the Marcus rate expression is a macroscopic summary of a microscopic stochastic logic, rooted in per-step probabilities rather than continuous deterministic evolution.

5. Interpreting Marcus Parameters in Iteration Space

Having reformulated Marcus electron transfer theory within an iteration-based framework, we can now reinterpret the meaning of its constituent parameters. Rather than describing the system as evolving over a continuous temporal coordinate, we treat the system as executing a sequence of discrete configuration-sampling events, each representing an attempt to reach the required energetic alignment for electron transfer. Within this causal and event-driven view, each Marcus parameter acquires a new physical meaning that is not time-centric but iteration-centric, and this reinterpretation offers fresh insights into how molecular systems actually function.

5.1 Attempt Frequency as 1/τ_iter

In traditional kinetics, the pre-exponential factor A in the Marcus rate equation is typically interpreted as an effective attempt frequency—a product of electronic coupling and vibrational or solvent relaxation terms. In the iteration-based framework, we identify this factor more precisely as:

$$A = \frac{1}{\tau_{\text{iter}}},$$

where τ_iter is the average time between statistically independent configuration-sampling events. These events are driven by the molecular system's intrinsic degrees of freedom—such as solvent reorganization, thermal vibrations, or protein conformational breathing. The assumption here is that each iteration is separated from the next by a characteristic timescale set by the rate of fluctuation of the nuclear environment. The system does not continuously evolve toward a transition state but makes discrete "attempts" to reach it through thermally activated fluctuations. This redefinition of A as 1/τ_iter foregrounds the event-based nature of molecular dynamics and separates time from causality: time becomes a property of how often iterations occur, not how the reaction unfolds deterministically.

5.2 Activation as a Logical Gate Condition

Traditionally, the concept of activation refers to overcoming an energetic barrier that separates reactants from products. In the iteration framework, activation is not a smooth climbing over a potential hill, but a logical gate condition: only configurations that meet strict energetic alignment criteria will allow electron transfer to proceed. Each iteration probes whether the current configuration satisfies the requirement for donor and acceptor energy degeneracy. If it does not, no transfer occurs and the system returns to sampling.

This interpretation shifts the role of activation from an energy landscape the system must traverse to a binary gate: the system either is or is not in the correct configuration for the reaction to proceed. Activation thus becomes a Boolean function over configuration space, evaluated at each iteration:

$$\text{Transfer occurs at iteration } n \iff E_{\text{donor}}(q_n) = E_{\text{acceptor}}(q_n).$$

This reconceptualization aligns activation with ideas in computation and logic circuits, where progress is conditional on satisfying specific criteria. It also allows us to handle more complex gating effects (e.g., conformational switching, redox state locking) in biological systems using iteration-based logic rather than time-based rate coefficients.

5.3 The Exponential Term as the Iteration Success Probability

In classical Marcus theory, the exponential term:

$$\exp\left(-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_B T}\right)$$

arises from the Boltzmann-weighted probability of the system reaching the activation geometry. In the iteration framework, this term is directly interpreted as the probability of success per iteration—i.e., the probability that a configuration sampled at random from the thermal ensemble results in successful electron transfer.

Thus:

$$P_{\text{succ}} = \exp\left(-\frac{\Delta G^{\ddagger}}{k_B T}\right) = \exp\left(-\frac{(\Delta G^{\circ} + \lambda)^2}{4\lambda k_B T}\right).$$

This success probability is independent of iteration number and intrinsic to the reaction landscape. The system may perform many iterations (unsuccessful attempts) before a successful one occurs. The rate of the overall process is determined not by how fast the system evolves in time, but by how frequently it samples and how rare success is on each attempt.

This redefinition removes the need to frame the reaction in terms of continuous trajectories. Instead, we see reaction rates as emerging from the balance of iteration frequency and per-iteration success, making the rate constant:

$$k_{\text{ET}} = \frac{1}{\tau_{\text{iter}}} \cdot P_{\text{succ}}.$$

5.4 Time as an Emergent Average Over Failed Attempts

The classical notion of reaction time—how long it takes for a system to go from reactant to product—is reinterpreted in this framework as the average number of failed iterations before success, multiplied by the average duration of each iteration. In other words, time emerges as a statistical quantity, not a fundamental variable.

Let N be the expected number of iterations required for success. Since each iteration is independent, the expected number is simply:

$$N = \frac{1}{P_{\text{succ}}}.$$

The average time for a successful reaction is therefore:

$$\langle t_{\text{reaction}} \rangle = \tau_{\text{iter}} \cdot N = \frac{\tau_{\text{iter}}}{P_{\text{succ}}}.$$

This result matches the standard definition of a first-order rate constant:

$$k_{\text{ET}} = \frac{1}{\langle t_{\text{reaction}} \rangle}.$$

But here, that rate is no longer a measure of smooth temporal progress—it is the product of two discrete, conceptually distinct components:

- The iteration interval (τ_{iter}): how often the system attempts to transfer.
- The iteration success probability (P_{succ}): how likely any attempt is to succeed.

Thus, time becomes a derived average over many causally unrelated attempts, each governed by system-specific logic rather than a continuous path toward activation. This view provides a deeper understanding of the probabilistic foundations of reaction rates and aligns with modern views of molecular dynamics as inherently discrete and stochastic.

6. Application to Biological Electron Transfer

Electron transfer in biological systems is highly evolved, temporally orchestrated, and often exhibits striking efficiency even in noisy, thermally fluctuating environments. Among the most extensively studied of these systems are the bacterial and plant photosynthetic reaction centers, where absorbed photons initiate rapid, directed charge separation across membranes. These multi-step processes have traditionally been described using time-resolved spectroscopies and fitted to multi-exponential decay models, yielding apparent “fast” and “slow” rate constants for various redox transitions. In this section, we apply the iteration-based framework to biological electron transfer, showing how it clarifies long-standing interpretive challenges, redefines the role of time, and naturally incorporates mechanisms such as gating, quenching, and recombination.

6.1 Photosynthetic Reaction Centers: Two-Photon Logic

Photosynthetic reaction centers (RCs), such as those in *Rhodobacter sphaeroides* or *Photosystem II*, operate through a series of discrete photochemical and redox events initiated by individual photons. The first photon excites the special pair of chlorophylls (P) to a singlet excited state (P*), which rapidly undergoes primary charge separation to produce a P^+ donor and a nearby reduced electron acceptor

(e.g., BPh^- or QA^-). A second photon is needed to drive the next electron transfer event, reducing QB and ultimately producing a stable quinol (QBH_2) product.

From an iteration-based perspective, each absorbed photon represents a distinct causal iteration, which either results in a productive redox step or fails due to the reaction center's current redox state. This leads to a two-photon logic gate, in which full turnover (i.e., quinol formation and release) requires two successful iterations in the correct redox and conformational context.

This logic-gated structure of the RC is obscured in time-based models, which treat all transitions as flowing continuously at rates determined by kinetic coefficients. By contrast, the iteration model makes clear that:

- One photon = one logical input
- Each iteration = one conditional attempt at charge transfer
- Product formation = the result of satisfying a multi-step conditional sequence

This not only enhances mechanistic understanding but opens the door to modeling RC behavior as a biochemical logic processor executing well-defined sequences of conditionally gated operations.

6.2 Reinterpreting "Slow" Reactions as Gated Iterations

One of the key interpretive challenges in RC kinetics is explaining why some steps—particularly those involving quinone binding, reduction, and release—occur on timescales many orders of magnitude slower than primary charge separation. In a time-based model, these are labeled "slow reactions" with rate-limiting constants derived from fits to decay curves. But this language often hides the causal structure of the process.

In the iteration framework, these "slow" reactions are not slow because the system is idle or waiting. Rather, the system is actively attempting to proceed at each iteration, but these attempts are gated by internal conditions:

- QB may already be reduced (not available for further electrons),
- The RC may not have undergone necessary conformational changes,
- A requisite proton transfer may not have occurred.

These conditions block progression even when photons are available, leading to repeated failed iterations. The effective slowness arises from low per-iteration success probability rather than from an intrinsically slow process.

This reinterpretation:

- Separates reaction readiness from photon flux or electron availability,
- Suggests that "slow" steps may be bottlenecked by availability, not by intrinsic rates,
- Predicts that altering the internal gating logic (via mutation, redox tuning, or environmental changes) may dramatically alter effective reaction rates without affecting electron mobility.

Thus, what is traditionally modeled as a long-lived intermediate or a slow step is now understood as a region of iteration space with a low probability of success, refining our ability to manipulate and engineer redox pathways in synthetic biology.

6.3 Implications for Gating, Quenching, and Recombination Dynamics

The iteration-based view also sheds new light on nonproductive processes such as quenching, charge recombination, and feedback gating that influence the efficiency and yield of biological electron transfer systems.

In classical models:

- Quenching is treated as a parallel decay pathway that competes with forward ET.
- Recombination is a back-reaction with its own rate constant.
- Gating is often implemented via phenomenological terms or complex kinetic networks.

In the iteration model, these are more naturally treated as conditional pathways embedded in the logic of each iteration:

- Quenching occurs if, during an iteration, the redox state of cofactors creates an energetic trap that absorbs the excitation energy or returns the system to ground state before charge separation.
- Recombination is the result of an iteration in which the electron returns from acceptor to donor due to misalignment or lack of downstream acceptor availability.
- Gating is implemented as a logical condition that determines whether an iteration is permitted to proceed (e.g., QB must be oxidized and correctly positioned for reduction to occur).

Each of these outcomes can be associated with a branch in the iteration logic tree, governed by the system's internal state variables. The total product yield then reflects the balance of successful forward iterations and these alternative pathways, each with their own probability-per-iteration rather than time-based rate.

In this view, RC efficiency becomes a function not of clock-time optimization but of maximizing successful causal paths through a branching sequence of probabilistic events. This opens a new approach to understanding and designing bio-inspired energy transduction systems—not by accelerating steps in time, but by restructuring the gating logic to favor productive iteration outcomes.

7. Theoretical and Experimental Implications

Recasting electron transfer and related redox processes as discrete, iteration-driven phenomena has both theoretical and experimental consequences that extend well beyond Marcus theory itself. By identifying the fundamental unit of biochemical action as a causal attempt rather than a segment of elapsed time, we realign the theoretical language of physical chemistry with the mechanistic logic observed in biological systems and increasingly mirrored in synthetic designs. This

shift allows us to unify molecular computation, stochastic thermodynamics, and redox biochemistry into a coherent modeling framework. It also points toward new classes of experimental observables and engineering strategies for manipulating biological and artificial electron transfer systems.

7.1 Bridging Molecular Computation and Physical Chemistry

The iteration-based framework naturally invites a comparison between electron transfer and molecular computation. In both cases, progress is conditional on satisfying specific internal states or input criteria, and each update (whether redox or logical) is a discrete causal event. By treating redox transitions as Boolean gates rather than continuous transitions along a potential energy surface, we frame biological processes as executing logical programs written into the structure and coupling of molecules.

This brings the language of physical chemistry into direct contact with emerging fields such as:

- DNA computing and enzyme logic gates,
- Quantum dot logic circuits,
- Synthetic biology signal transduction networks,
- Thermodynamic computing models where computation is explicitly energy-driven.

Importantly, this interpretation does not replace thermodynamics—it completes it by revealing its event-structured, conditional underpinnings. Marcus' exponential emerges not from a smooth climb over an energy barrier but from the statistical rarity of achieving logical alignment in high-dimensional configuration space. This reinforces the notion that energy and information are inseparable at the molecular scale, and that redox chemistry is as much about decision-making as it is about motion.

7.2 Testable Predictions: Stepwise Logic vs. Rate-Smeared Time

One of the strongest motivations for adopting an iteration-based view is that it offers experimentally testable predictions that diverge from traditional rate-based models, especially at the single-molecule or low-flux limit. Some key experimental consequences include:

- Burst statistics in single-molecule redox experiments:
  Iteration-based logic predicts that reactions will occur in stepwise bursts separated by variable periods of failed or gated attempts, rather than following smooth Poisson or exponential waiting-time distributions.
- Photon-counting regimes in photosynthetic centers:
  At low light intensities, reaction centers will show behavior dominated by discrete photon-triggered state transitions, with performance that deviates significantly from average rate models.
- State-dependent recombination dynamics:
  If recombination is a function of gating state rather than time delay, its probability should correlate with structural markers (e.g., quinone occupancy, conformational changes) rather than elapsed time alone.
- Response to perturbation:
  If a redox step is slowed by mutation or environmental change, iteration-based modeling predicts that this will alter the logic tree of success/failure more than simply reducing a rate constant. This leads to nonlinear responses not predicted by classical kinetics.

Emerging technologies such as single-molecule FRET, time-resolved cryoEM, optical trapping, and quantum dot blinking statistics are ideally suited to test these predictions by tracking redox state transitions as discrete, time-tagged events with known photon or voltage inputs.

7.3 Implications for Artificial Photosystems and Redox Networks

From a design perspective, the iteration-based model offers a new blueprint for constructing artificial systems that mimic or even improve upon biological redox

efficiency. In current efforts to build synthetic photosynthetic units, molecular solar fuels platforms, or redox-based computation, engineering is often approached through control of energy levels, material interfaces, or coupling constants—all based on classical, time-continuous reaction models.

By contrast, the iteration model suggests that performance optimization may depend critically on:

- Reducing the number of blocked or stalled iterations by adjusting gating logic (e.g., cofactor placement, product release rates),
- Separating logic paths for charge separation and recombination by introducing conditional filters (e.g., dynamic allosteric controls),
- Programming redox logic trees that direct charge through productive paths based on internal molecular state rather than energy gradients alone.

Artificial photosystems that mimic biological gating—such as requiring two sequential photon events or using conformational gating to protect against recombination—can be explicitly modeled as logic circuits. This encourages a design philosophy where devices are constructed not just to move charge quickly, but to compute efficiently in chemical space. Redox pathways become synthetic algorithms, executed one iteration at a time.

This paradigm invites a deeper fusion of chemistry, information theory, and computation, and suggests that some of the most powerful machines in biology—the photosystems, mitochondrial chains, and nitrogenases—are best understood not merely as catalysts, but as molecular processors implementing compact, iteration-based logic over thermodynamic landscapes.

8. Conclusion

The classical framework of chemical kinetics, particularly as exemplified by Marcus theory, has provided profound insight into the thermodynamic and structural principles governing electron transfer. Yet it remains couched in a temporal language—one that treats molecular processes as evolving smoothly over time,

with rate constants serving as bridges between thermodynamic states. In this paper, we have proposed a fundamental reinterpretation: that electron transfer and related molecular phenomena are more naturally and accurately described as sequences of discrete, iteration-based events, each representing an attempt to satisfy a conditional energetic criterion. From this perspective, the appearance of time and rate arises only as a macroscopic statistical average over many such iterations.

8.1 From Probabilistic Thermodynamics to Biochemical Logic

At the heart of this shift is a redefinition of causality in molecular systems. Rather than visualizing reactions as continuous trajectories across energy landscapes, we view them as stochastic sampling operations governed by underlying logical rules. Thermodynamic parameters such as reorganization energy and free energy change no longer serve as dynamic coordinates, but instead as filters on configuration space, determining the likelihood of success per iteration. Activation becomes a Boolean condition; reorganization energy becomes a measure of how tightly constrained the success zone is within the ensemble of thermally accessible configurations.

This reframing repositions molecular dynamics within the broader context of information theory and computation, enabling redox systems to be interpreted not only as energy transducers, but as causal processors, executing biochemical logic gates that respond to environmental and internal molecular states. It aligns well with growing interest in the computing capacity of biological molecules, from ribozymes to allosteric proteins, and invites a fusion of thermodynamic and computational models of living systems.

8.2 Marcus Theory as an Emergent Property of Iteration

Crucially, we have shown that Marcus theory is not invalidated by this reinterpretation—it is recovered as a natural consequence of iteration-based sampling. The exponential rate law, long interpreted as a reflection of barrier crossing under continuous thermal motion, arises from the probability of a successful alignment event per iteration. The rate constant k_{ET} is redefined as:

$$k_{\mathrm{ET}} = \frac{1}{\tau_{\mathrm{iter}}} \cdot \exp\left(-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_B T}\right),$$

where τ_iter represents the time between independent configuration samples, and the exponential term reflects the rarity of success under thermal fluctuations. This product form is not arbitrary but grounded in the logic of discrete event sampling. Each parameter in Marcus theory finds a direct analog in iteration space: attempt frequency, gating logic, and success probability. Time, so central to traditional modeling, becomes derivative, an emergent average over iteration statistics.

8.3 Toward a Universal Iteration-Based Kinetic Framework

The implications of this shift are not limited to electron transfer. Any system governed by conditional molecular events—ligand binding, enzymatic catalysis, signal transduction, or conformational switching—can be recast in terms of discrete iterations. This offers a universal framework for biochemical kinetics as stepwise logic, uniting probabilistic thermodynamics with causal modeling. Rate constants become measurable outcomes of two distinct features: the frequency of independent sampling attempts, and the probability that any given attempt succeeds.

This framework is especially powerful in systems where traditional time-based models struggle:

- Single-molecule experiments,
- Low-photon or low-substrate regimes,
- Enzyme networks with allosteric gating,
- Synthetic logic systems and molecular computers.

By embracing iteration as the foundational unit of biochemical change, we align molecular theory with both experimental resolution and the logic-rich behavior of biological systems. The result is not a rejection of classical kinetics, but its completion: a framework in which Marcus theory becomes a special case of a

deeper, discrete model of molecular decision-making. In doing so, we open new pathways for understanding, designing, and engineering the computational potential of chemistry itself.

Epilogue: Iteration-Based Formulation of Michaelis–Menten Kinetics

Throughout this paper, we have recast classical rate theories—particularly Marcus electron transfer theory—within a framework that treats molecular processes as sequences of discrete, condition-dependent iterations rather than continuous-time flows. This logic is equally applicable to enzymatic catalysis, where reaction progress is typically modeled by differential equations describing substrate consumption and product formation over time. In standard Michaelis–Menten kinetics, the rate of product formation is expressed as:

$$v(t) = \frac{V_{\max}[S](t)}{K_M + [S](t)},$$

where $v(t) = d[P]/dt$, $V_{\max} = k_{\text{cat}}[E]_0$, and K_M is the Michaelis constant. However, this expression presumes continuous time evolution and obscures the stepwise molecular decisions carried out by the enzyme.

In the iteration-based framework, we reinterpret enzyme catalysis as a sequence of discrete turnover attempts, indexed by an integer nnn, where each iteration represents a complete cycle of binding, catalysis, and product release. The enzyme either succeeds in catalyzing the reaction at step nnn, or it does not, depending on the substrate concentration at that point.

Let $[S]_n$ denote the substrate concentration at the n^{th} iteration, and let δ represent the incremental product formed per iteration (typically one molecule per active site). The per-iteration efficiency is defined as:

$$\eta_n = \frac{[S]_n}{K_M + [S]_n},$$

which mirrors the classic Michaelis–Menten fraction but reinterpreted as a probability of catalytic success per iteration.

The cumulative product formed after n iterations is then:

$$[P]_n = \sum_{k=1}^{n} \eta_k \cdot \delta.$$

Under conditions of negligible substrate depletion, this simplifies to:

$$[P]_n \approx n \cdot \delta \cdot \frac{[S]_0}{K_M + [S]_0},$$

which yields a linear relation between iteration number and product formed, modulated by the Michaelis–Menten ratio evaluated at the initial substrate concentration.

In this formulation:

- K_M becomes the substrate concentration at which the per-iteration success probability is 50%,
- k_{cat} is reinterpreted as the **inverse of the average time per successful iteration**, and
- The enzyme's activity is governed not by continuous rates but by **discrete success probabilities conditioned on state variables**.

This epilogue demonstrates that the iteration-based formalism not only recovers the structure of classic enzymology but offers a more fundamental and flexible representation of biochemical logic—one that places molecular causality, not time, at the center of kinetic theory.

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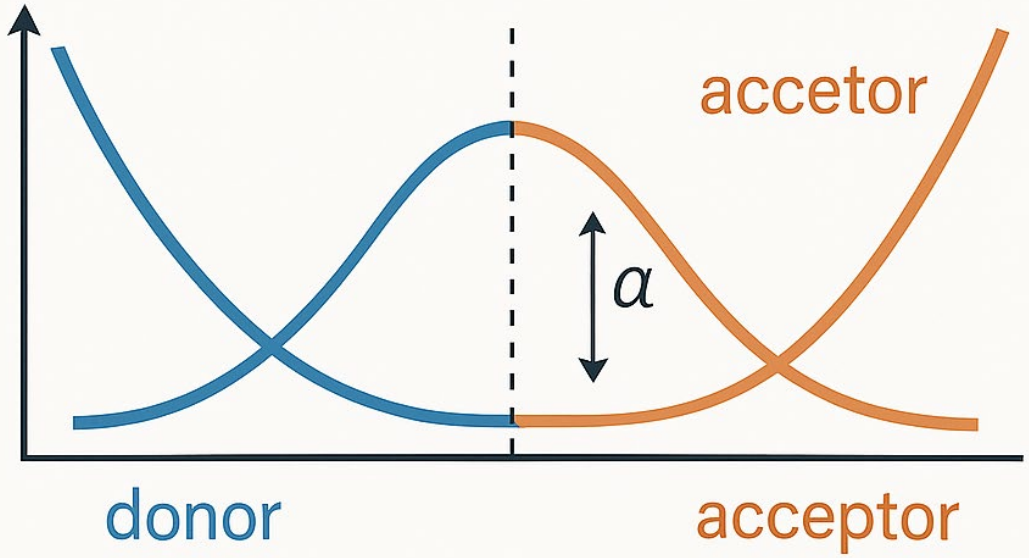
Marcus electron transfer theory



Iteration