Marcus classical theory

Rudolph A. Marcus developed an original theory to explain the rate of ET reactions, linking the thermodynamics of the process to its kinetics. It was originally formulated to address outer sphere electron transfer reactions.

His original article (1956) referred to the self exchange reaction in aqueous solution $\text{Fe}^{2+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{2+}$, where the reorganization energy is solely due to reorganization of water dipoles around solvated ions.

Based on statistical mechanics considerations, Marcus theory postulates that:

- a) Both precursor and successor states can be described by parabolic potential curves of similar shape and widths
- b) Nuclear reorganization proceeds \textit{classically} through low frequency vibrational and rotational modes
- c) Nuclear reorganization is kinetically "symmetrical" with $k_n = k_{-n}$.
Geometrical derivation of Marcus equation

Parabolas:
\[ y_i = ax^2 \]
\[ y_f = a(x + b)^2 + c \]

Intersection \((x^\dagger, y^\dagger)\):
\[ y^\dagger = a(x^\dagger)^2 = a(x^\dagger + b)^2 + c \]
\[ a(x^\dagger)^2 = a(x^\dagger)^2 + 2 abx^\dagger + (ab^2 + c) \]
\[ 2 abx^\dagger = - ab^2 - c \]
\[ x^\dagger = \frac{-(ab^2 + c)}{2 ab} \]
\[ y^\dagger = a(x^\dagger)^2 = \frac{(ab^2 + c)^2}{4 ab^2} \]

\[ \Lambda = ab^2 \]
\[ \Delta r G^0 = c \]
\[ \Delta G^\dagger = y^\dagger \]

\[ \Delta G^\dagger = \frac{(\Lambda + \Delta r G^0)^2}{4 \Lambda} \]
**Marcus-Hush theory**

Marcus theory was further extended to inner sphere electron transfer reactions by Noel Hush. Parabolic potential energy curves were derived in this case from harmonic oscillator potentials. The final formulation is practically identical to Marcus' (Hush's formulation is known as Marcus-Hush theory) and reads:

\[ \Delta G^\dagger = \frac{(\Lambda + \Delta r G^0)^2}{4\Lambda} \]

For an excellent review of the theory, see for instance:

Activation energy ($\Delta G^\ddagger$) dependence upon exoergicity ($\Delta rG^0$) of ET

\[-\Delta rG^0 < \Lambda\]

\[-\Delta rG^0 = \Lambda\]

\[-\Delta rG^0 > \Lambda\]

$\Delta rG^0 = G_f - G_i$
Avoided crossing of potential energy surfaces

In order for electron transfer to occur, an overlap between the populated orbital of the donor and the empty orbital of the acceptor is necessary in the activated complex. This electronic interaction involves a split of electronic energy levels.

If the electronic states are of the same symmetry, breakage of the Frank-Condon principle at the saddle point causes in turn a split of potential energy levels and avoided crossing of the two curves.

As a result two potential surfaces are created that are separated at the configuration of the activated complex by an energy gap $2|H_{DA}|$. $|H_{DA}|$ is a matrix element for electronic coupling between the donor and the acceptor.
Adiabatic vs. diabatic electron transfer

In an adiabatic electron transfer process ($|H_{DA}| >> k_BT$) the reacting system remains on the lowest potential energy surface in passing from reactants to products. The activation-controlled rate constant $k_{et}$ is related to the activation energy by Eyring's equation:

$$k_{et} = \nu_n \cdot \exp\left(-\frac{\Delta G^i}{k_BT}\right)$$

$\nu_n$ is the nuclear reorganization frequency of the precursor complex. In the simplest model, $\nu_n = k_BT / h$.

When the electronic coupling is sufficiently small ($|H_{DA}| \leq 3 k_BT$), the precursor complex can borrow some thermal energy from the environment and jump from one potential energy curve to the other. The rate of the diabatic (or non-adiabatic) electron transfer process in this case is reduced considerably and is not governed by the sole nuclear reorganization rate $\nu_n$ anymore. A treatment of the problem will be proposed later in the course (p. 33).
Marcus' quadratic equation predicts some counter-intuitive kinetic behavior as the driving force becomes larger than the reorganization energy ($-\Delta r G^0 > \Lambda$):

The theoretical value of the activation energy $\Delta G^\dagger$ starts to raise again, hence reducing the overall ET process rate constant $k_{et}$.

The predicted existence of such an "inverted region" was controversial from the time the theory was proposed in 1956 until experimental evidence of it was found for a set of photoredox reactions (Closs & Miller, 1986).
Marcus vs. Tafel equation

In electrochemistry, Butler-Volmer's equation relates the current density $j$ through an electrode to the overpotential $\eta$, defined as the difference between the electrode potential and the standard potential of the redox couple in solution. If the process is controlled by activation, the current density $j$ is proportional to the rate of electron transfer reaction at the interface and, therefore, to its first order rate constant $k_{et}$. Butler-Volmer's equation simplifies for $\eta \ll 0$, yielding Tafel's linear equation:

$$\ln k_{et} = \ln k_{et}^0 - \frac{\alpha F}{RT} \eta_c$$

where $k_{et}^0$ represents the rate constant of electron transfer in reversible conditions ($\eta = 0$), $\alpha$ is a symmetry- or configuration coefficient and $F$ is the Faraday constant.

Provided the value of the symmetry coefficient is set to $\alpha = 0.5$, Tafel's linear equation is compatible with Marcus' parabolic relationship for $-\Delta_{et}G^0 \ll \Lambda$. 

![Graph showing the comparison between Tafel and Marcus curves](image-url)
**Nuclear reorganization energy $\Lambda$**

Commonly the total reorganization energy $\Lambda$ is expressed as the sum of an inner-shell contribution $\lambda_{in}$ (also sometime written $\lambda_v$) accounting for vibrational reorganization of the redox partners and an outer-shell contribution $\lambda_{out}$ (also sometime written $\lambda_s$) attributed to the reorganization of the solvent dipoles:

$$\Lambda = \lambda_{in} + \lambda_{out} \quad (always > 0)$$

Approximations have been proposed to calculate the value of $\lambda_{out}$ taking into account the dielectric constant $\varepsilon$ (relative permittivity) of the solvent:

$$\lambda_{out} = \frac{(\Delta e)^2}{4\pi \cdot \varepsilon_0} \cdot \left(\frac{1}{d_D} + \frac{1}{d_A} + \frac{1}{r_m}\right) \cdot \left(\frac{1}{n^2} - \frac{1}{\varepsilon}\right) \quad \text{(homogeneous system)}$$

$$\lambda_{out} = \frac{(\Delta e)^2}{8\pi \cdot \varepsilon_0} \cdot \left(\frac{2}{d} - \frac{1}{2 \cdot r_m}\right) \cdot \left(\frac{1}{n^2} - \frac{1}{\varepsilon}\right) \quad \text{(heterogeneous system)}$$

- $e$: elementary charge
- $d$: diameter of the reactant species
- $r_m$: optimum reaction distance
- $\varepsilon$: static dielectric constant of the solvent
- $n$: solvent refractive index. $n^2$ represents the optical (high frequency) dielectric constant of the medium.
**Exercise 7.3**

A strongly emissive neutral perylene dye (S) dissolved in ethanol has a fluorescence quantum yield $\Phi_f = 0.90$. The lifetime of its excited state is $\tau = 50$ ns.

In the presence of tri-ethylamine (TEA) electron donor in large concentration ($\sim 1$ M), the fluorescence of the dye is quenched down to $\Phi_f \approx 0.01$.

Estimate the inner-sphere reorganization energy $\lambda_{in}$ [eV] associated to the light-induced electron transfer taking place between $S^*$ and TEA.

**Numerical data**

$\phi^0 (S/ S^-) = -1.0$ V / SCE

$\phi^0 (TEA^+/ TEA) = +0.7$ V / SCE

$\Delta E_{0,0} (S) = 2.5$ eV

$n (EtOH) = 1.3611$

$\varepsilon (EtOH) = 24.3$

$\varepsilon_0 = 8.86 \cdot 10^{-12}$ A $\cdot$ s V$^{-1}$ $\cdot$ m$^{-1}$ (dielectric permittivity of vacuum)
Fermi's golden rule for diabatic ET

The general expression describing the rate of non-adiabatic ET processes is given by Fermi's golden rule:

\[ k_{et} = \frac{2\pi}{\hbar} \cdot |H_{DA}|^2 \cdot \rho(E_f) \]

This relation applies to all non-adiabatic processes and is based on the Born-Oppenheimer approximation decoupling electronic and nuclear contributions. It includes the electronic coupling matrix element squared \(|H_{DA}|^2\) (with the dimensions of an energy). \(|H_{DA}|\) depends on the overlap of the electronic wave functions of the donor and the acceptor and thus upon the distance \(r\), on which electron tunneling takes place:

\[ |H_{DA}|^2 = |H_{DA}|^2 (r = r_0) \cdot \exp [-\beta \cdot (r - r_0)] \]

\(\beta\) is a damping factor, whose value is typically <1.2 Å\(^{-1}\) for through-space ET.

\(\rho(E_f)\) is a Franck-Condon factor-weighted density of states. It expresses the contribution of nuclear reorganization to the electron transfer rate. The \(\rho(E_f)\) term is proportional to the matrix element describing the overlap of nuclear wave functions of vibronic states of the precursor and successor complexes.
Nuclear factor of Fermi's golden rule

\[ \rho(E_f) = \sum_v \sum_w \rho_v \cdot |< \chi_i | \chi_f >|^2 \cdot \delta(E_{iw} - E_{fw}) \]

\[ \Delta \rho = \Lambda + \Delta G^0 \]

Classical limit

If nuclear reorganization proceeds only through low frequency rotational and vibrational modes, quantum levels are so close that they form a quasi-continuum of states.

\[ \rho(E_f) = \frac{1}{\sqrt{4\pi \cdot \Lambda \cdot k_B T}} \cdot \exp \left( -\frac{\Delta G^\dagger}{k_B T} \right) \]

\[ \Delta G^\dagger = \frac{(\Lambda + \Delta G^0)^2}{4\Lambda} \]

(equivalent to Marcus' equation)
Marcus-Jortner semi-classical theory

When nuclear reorganization proceeds through high frequency vibrational modes, a nuclear tunneling effect cannot be neglected. This quantum treatment is applied to high frequency modes, while a classical treatment is still applied to low frequency modes, such as those associated to the solvent dipoles rotational reorganization (Marcus-Jortner semi-classical theory).

In the simplified case, where only a single vibrational frequency $\nu$ is considered (single-phonon model), the Fermi golden rule can be expressed by the Marcus-Dogonadze equation:

$$k_{et} = \left| H_{DA} \right|^2 \cdot \frac{1}{\sqrt{2\pi} \cdot \lambda_{out} \cdot k_B T} \cdot \exp \left( \frac{-\lambda_{in}}{\nu} \right) \cdot \sum_{n=0}^{\infty} \frac{\left( \frac{\lambda_{in}}{\nu} \right)^n}{n!} \cdot \exp \left[ -\frac{(\Delta G_r^0 + n\nu + \lambda_{out})^2}{4 \lambda_{out} \cdot k_B T} \right]$$

When the values of $\lambda_{in}$ or $\nu$ are small, the equation is reduced back to the Marcus classical result. As well, when the overlap between vibrational wave functions of initial and final states is weak, the nuclear tunneling effect becomes negligible, even if high frequency reorganization modes associated to the electron transfer do exist.
Semi-classical treatment of electron transfer

Simple considerations, such as illustrated by the scheme here below, show that efficient vibrational coupling and nuclear tunneling take place more specifically in the Marcus inverted situation (right). The semi-classical treatment is therefore necessary in the inverted region, while the classical approach is sufficient in the normal region.
Semi-classical treatment of electron transfer

\[ k_{et} = \left| H_{DA} \right|^2 \cdot \frac{1}{\sqrt{2\pi \cdot \Lambda_{out} \cdot k_B T}} \cdot \exp \left( -\frac{\lambda_{in}}{\hbar \nu} \right) \cdot \sum_{n=0}^{\infty} \left( \frac{\lambda_{in}}{\hbar \nu} \right)^n \cdot \exp \left[ -\left( \Delta G^0_r + n\hbar \nu + \Lambda_{out} \right)^2 \right] \]
**Temperature-dependence of ET kinetics**

Nuclear tunneling in the inverted region means that electron transfer does not proceed over the activation energy barrier $\Delta G^\dagger$. The Marcus-Dogonadze equation thus predicts ET does not follow Arrhenius' law and that $k_{et}$ does not depend upon temperature in the inverted region.
Charge injection into a continuum of acceptor states

Photoinduced electron transfer from a dye excited state \( S^* \) into the conduction band of a semiconductor \( S^* + SC \rightarrow S^+ + e^-_{cb} \) (SC) is called **charge injection**. In this case the acceptor is not represented by a discrete electronic level but by a continuum of empty states. \( \Delta r G^0 \) of the reaction is not well defined and an activation-less ET process is usually possible.
Charge injection into a continuum of acceptor states

Because overlap of nuclear wave functions in the precursor and successor complexes is optimum in the case of a continuum of acceptor levels, the nuclear factor $\rho(E_f)$ is always very large. Fermi's golden rule reduces then to:

$$\rho(E_f) \approx n_a \cdot \frac{1}{\hbar \omega}$$

$\rho(E_f)$ is the nuclear factor, $n_a \cdot \frac{1}{\hbar \omega}$ is the density of vibrational product states. $n_a (0 \leq n_a \leq 1)$ is the reduced density of electronic acceptor states in the semiconductor's conduction band. $1/\hbar \omega$ is the density of vibrational product states.

Note that, in such a situation, the electron transfer rate does not depend upon $T$ nor $\Delta r G^0$ anymore. Two parameters are now essentially controlling the injection rate $k_{et}$: the density of acceptor states in the conduction band and the electronic coupling factor $|H_{DA}|^2$. 

$$k_{et} = \frac{2\pi}{\hbar} \cdot |H_{DA}|^2 \cdot \frac{n_a}{\hbar \omega}$$
Dynamics of light-induced electron transfer

In practical applications of photo-induced ET reactions, charge separation has to be maintained during a period of time sufficient for further redox reactions to take place. Ideally, forward ET involving an excited state has to be as fast as possible, while back electron transfer during which charges recombine has to be slow.

Such an ideal situation is achieved when the energetics of the system implies activation-less forward ET and very exoergic back ET process situated in the inverted Marcus region.