Fotoquímica

Aula 5 e 6

Transferência de Energia e Transferência de Elétron

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Caminhos de espécies fotoexcitadas

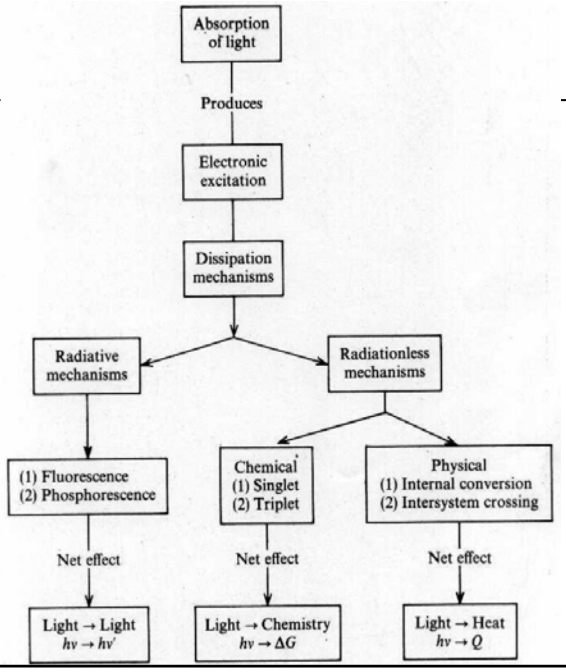
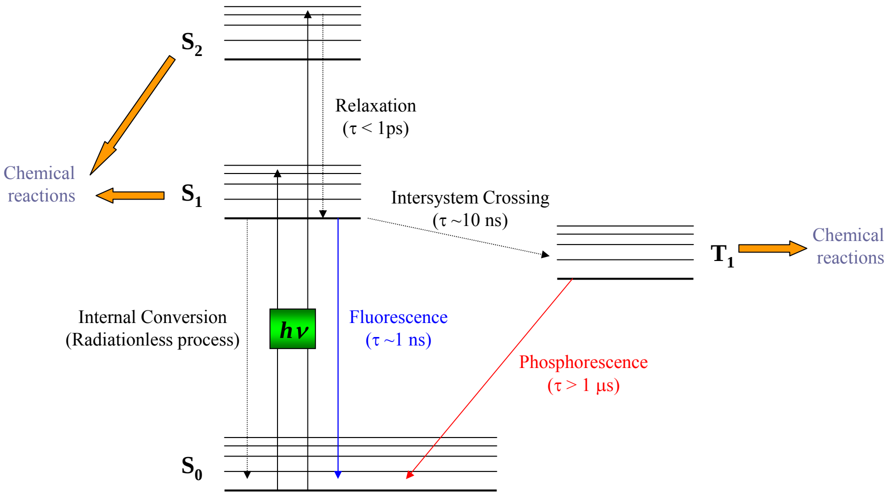


Diagrama de Jablonski



Estado Fundamental: o mais baixo, não excitado, estado eletrônico de um átomo ou molécula

Transferência de energia intermolecular

$$D^* + A \rightarrow D + A^*$$

Donor Acceptor

E- Etransfer – both D* and A* are electronically excited.

Often referred to as “quenching” as it removes excess electronic energy of initially excited molecule.

fotosensitização de A (aceptor) ou inibição de D (doador)
D é o sensitizador e A é o inibidor ou *quencher*

Transferência de energia intermolecular

* Electronic energy transfer

Radiative : trivial mechanism

Non-radiative

coulombic : 50 Å, long-range

electron-exchange : 10~15 Å

Energy and electron transfer nomenclature

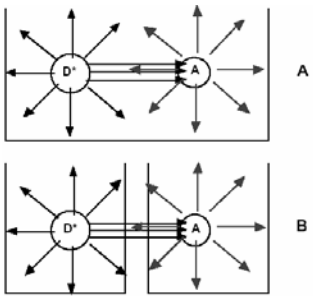
$D^+ + A \rightarrow D + A^+$ **hole transfer**

$D^- + A \rightarrow D + A^-$ **electron transfer**

$D^* + A \rightarrow D + A^*$ **energy transfer**

Trivial mechanism for energy transfer

(radiative emission-absorption energy transfer)



Trivial energy transfer between D^* and A, with A^* emitting following absorption of emission by D^*. Part B emphasizes the independence of emission and absorption by noting that D and A could be in different containers.

$$\mathbf{D^*} \rightarrow \mathbf{D} + h\nu$$
$$h\nu + \mathbf{A} \rightarrow \mathbf{A^*}$$

The "trivial" mechanism requires that D^* emits photons which A is capable of absorbing. The rate or probability per unit time of energy transfer from D^* to produce A^* will depend on:

- High quantum yield for emission from D^* — ϕ_e^D
- High concentration of A — [A]
- High extinction coefficient for A — ε_A
- Overlap of emission from D* and absorption from A — $J = \int_0^\infty I_D \, \varepsilon_A \, d\tilde{\nu}$

Radiative transfer

$D^* \rightarrow D + h\nu$

$h\nu + A \rightarrow A^*$

$$Rate = k_{fl}^{D} P_{abs}^{A} [D^*]$$

- Long range
- Overlap of absorption and emission spectra

$$P_{abs}^{A} \propto [A] l \int_{0}^{\infty} F_D(\nu) \varepsilon_A(\nu) d\nu$$

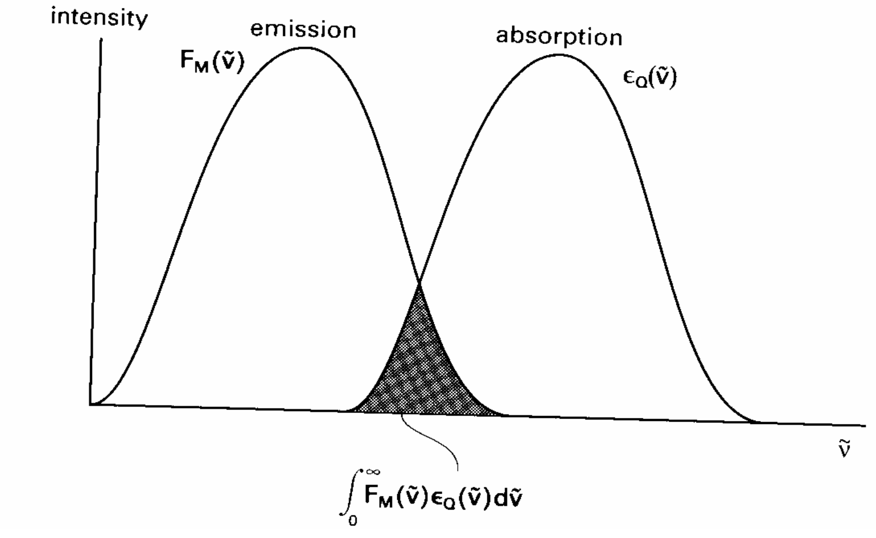
P_{abs}^{A} - probability of absorption of A

$F_D(\nu)$ – spectral distribution of donor emission

$\varepsilon_A(\nu)$ – molar absorption coefficient of acceptor

ℓ - path length of absorption

Overlap of absorption spectrum of A and emission spectrum of D



Non-radiative mechanism

A + D* → [AD*] → [A*D] → A* + D

- Formation of collision complex
- Intramolecular energy transfer within complex

$$k = \frac{2\pi}{\hbar}\left|\int \Psi^{*}_{A^{*}D} H' \Psi_{AD^{*}}\right|^{2} \rho(E)$$

$$\Psi_{A^{*}D} = \Psi_{A^{*}}\Psi_{D} \qquad \Psi_{AD^{*}} = \Psi_{A}\Psi_{D^{*}}$$

- H' is perturbation due to intermolecular forces (Coulombic, long range – "Forster") or electronic orbital overlap (exchange, short range – "Dexter")

Long Range (Forster) energy transfer

There will be a critical distance r_0 at which the rate of energy transfer is equal to the rate of decay of fluorescence of D (Typically r_0 = 20 – 50 Å)

At this point $k_T = 1/\tau_D$. At any other distance,

$$k_T = \tau_D^{-1}\left(\frac{r_0}{r}\right)^{6} \qquad r_0^{6} = \frac{0.529\Phi_f^D \kappa^2}{n^4 N_A}\int_0^\infty F_D(\nu)\varepsilon_A(\nu)\frac{d\nu}{\nu^4}$$

Note $\Phi_f^D \tau_D^{-1}$ is equal to the fluorescence rate constant for D.

Short range energy transfer (Dexter)

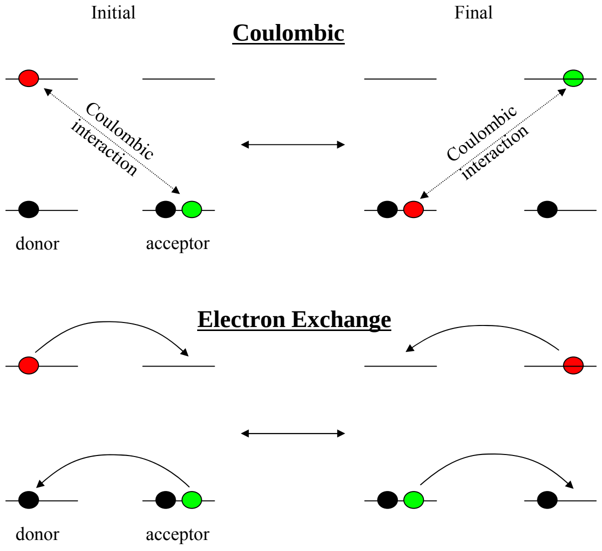
- Exchange interaction; overlap of wavefunctions of A and D

$$k_T(exchange) \propto \exp(-2r_{DA}/L)$$

L is the sum of the van der Waals radii of donor and acceptor

- Occurs over separations ≈ collision diameter
- Typically occurs via exciplex formation (see below)

Comparison of the Coulombic and Exchange mechanisms of electronic energy transfer



In Coulombic energy transfer no electrons "change molecules", but rather two transitions occur simultaneously in a process that could be described as the transfer of a "virtual photon"; Since no electrons are actually transferred in the Coulombic mechanism, it is clear that this process cannot have an analogy in the case of electron transfer.

Endotermic and exotermic energy transfer

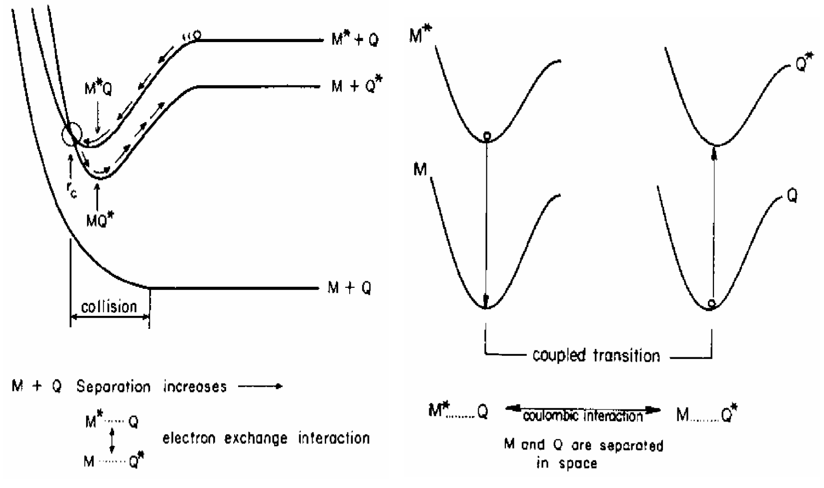
A eficiência da transferência de energia depende das configurações do *spin* e das energias relativas dos estados excitados de D e A.

- **transferência endotérmica**: E(A*) > E(D*). Mesmo permitida pelo *spin*, a transferência é <u>impossível</u> pelo mecanismo dipolo-dipolo que requer acoplamento entre uma transição de A envolvendo absorção de energia com uma transição de D* envolvendo emissão de energia. É <u>ineficiente</u> pelo mecanismo de troca, devido à possível reversibilidade do processo (transferência A*→D é exotérmica).

- **transferência exotérmica**: E(A*) < E(D*). Se permitida pelo *spin*, é usualmente <u>eficiente</u> e pode ocorrer pelo mecanismo dipolo-dipolo ou pelo mecanismo de troca.

Schematic surface representation of collisional energy transfer

$$M^* + Q \rightarrow M + Q^*$$



Energy transfer

transferência singlete-singlete
(mecanismo dipolo-dipolo e de troca)

$$D^*(S_1) + A(S_0) \rightarrow D(S_0) + A^*(S_1)$$

transferência triplete-singlete
(proibida pelo *spin* - rara)

$$D^*(T_1) + A(S_0) \rightarrow D(S_0) + A^*(S_1)$$

transferência triplete-triplete
(freqüente - somente mecanismo de troca)

$$D^*(T_1) + A(S_0) \rightarrow D(S_0) + A^*(T_1)$$

Energy transfer: triplete-triplete

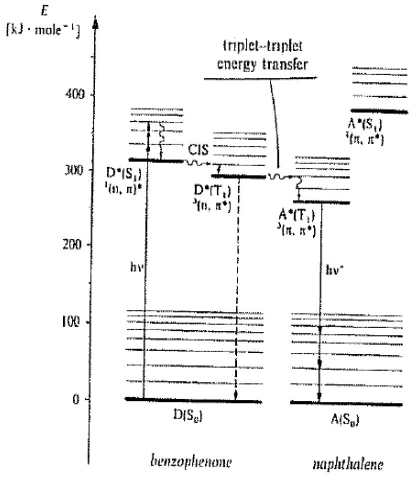


Figure 1.14 Triplet–triplet energy transfer between *benzophenone* (D) and *naphthalene* (A)

Energy transfer: triplete-triplete

- Diffusional Encounter:

  $D + A \qquad\qquad DA$

- Electron Transfer:

  $DA \rightarrow D^{+}A^{-}$

- Diffusional Separation:

  $D^{+}A^{-} \qquad\qquad D^{+} + A^{-}$

- Back Electron Transfer:

  $D^{+}A^{-} \rightarrow DA$

Dynamics of electron transfer

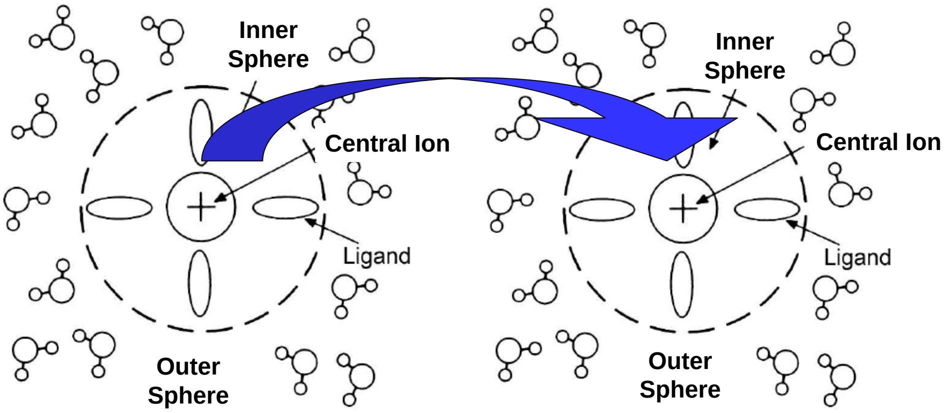
The rate of electron transfer depends on:

(1) the distance between the electron donor and acceptor;

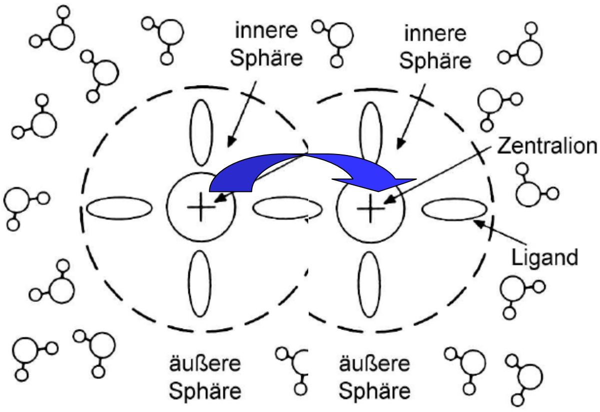
(2) standard Gibbs free energy change of the reaction;

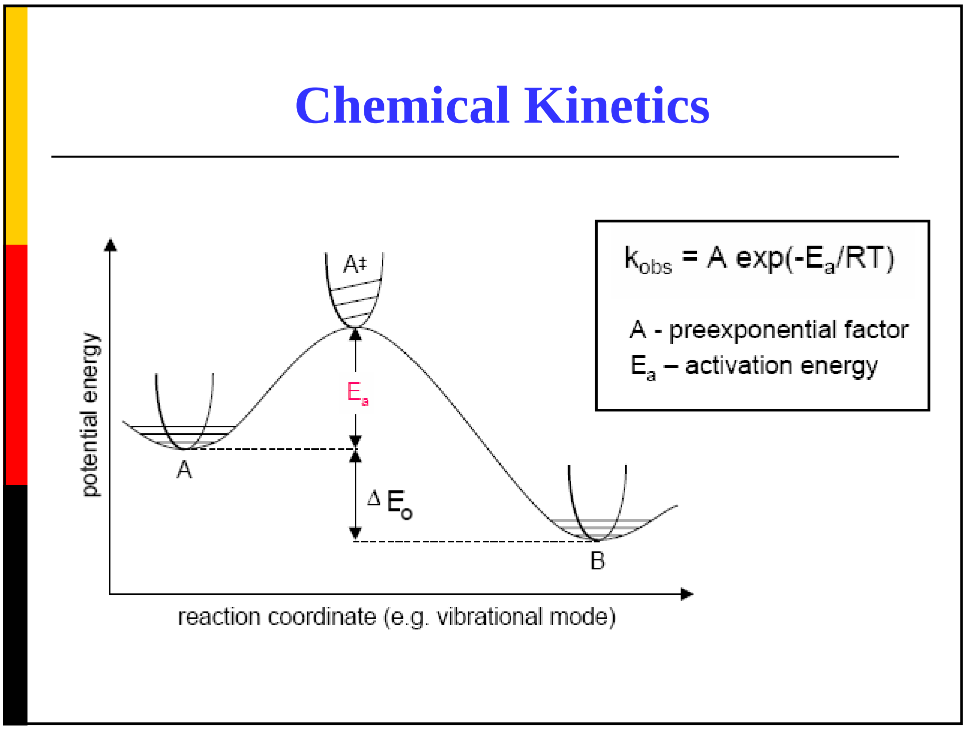
(3) the energy associated with molecular rearrangements.

OUTER SPHERE Electron Transfer



INNER SPHERE Electron Transfer



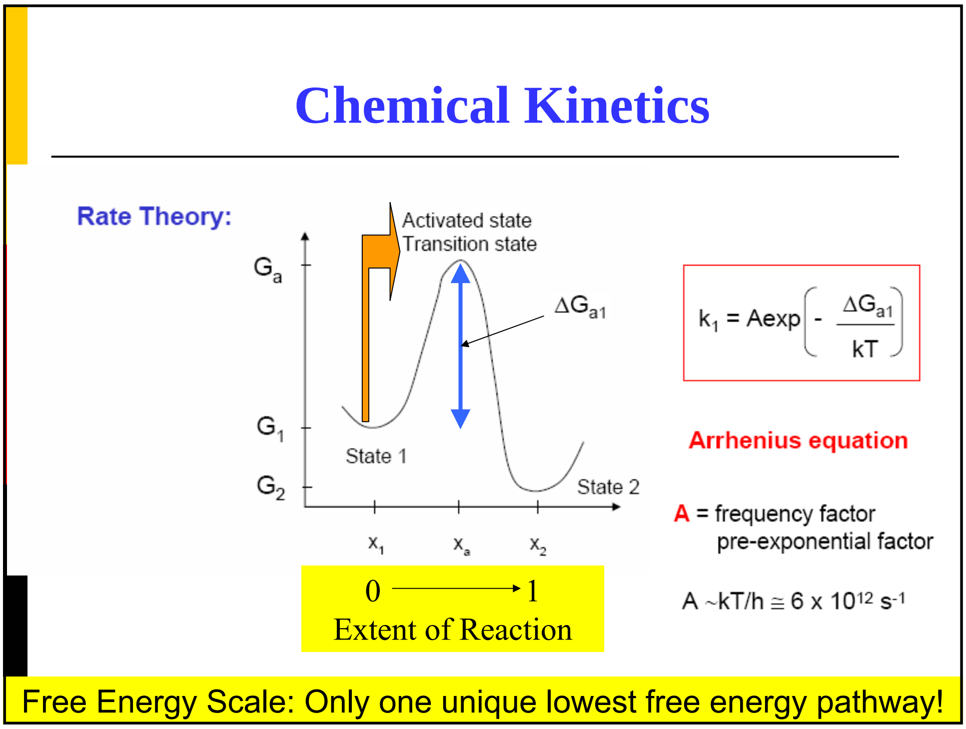


Chemical Kinetics

$k_{obs} = A\ \exp(-E_a/RT)$

A - preexponential factor

E_a – activation energy



Chemical Kinetics

Rate Theory:

$$k_1 = A\exp\left(-\frac{\Delta G_{a1}}{kT}\right)$$

Arrhenius equation

A = frequency factor
pre-exponential factor

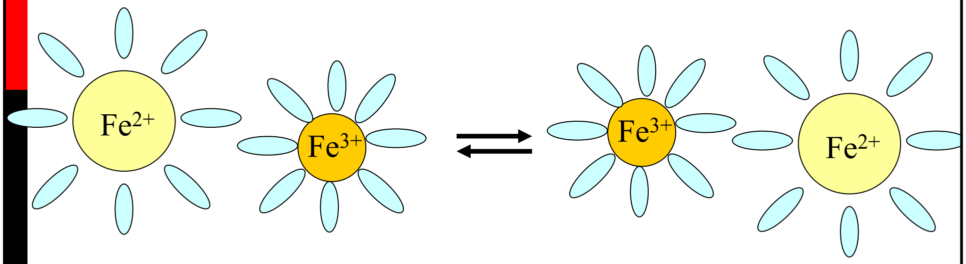
A ~kT/h ≅ 6 x 10^{12} s^{-1}

Free Energy Scale: Only one unique lowest free energy pathway!

Self-Exchange Electron Transfer Reaction

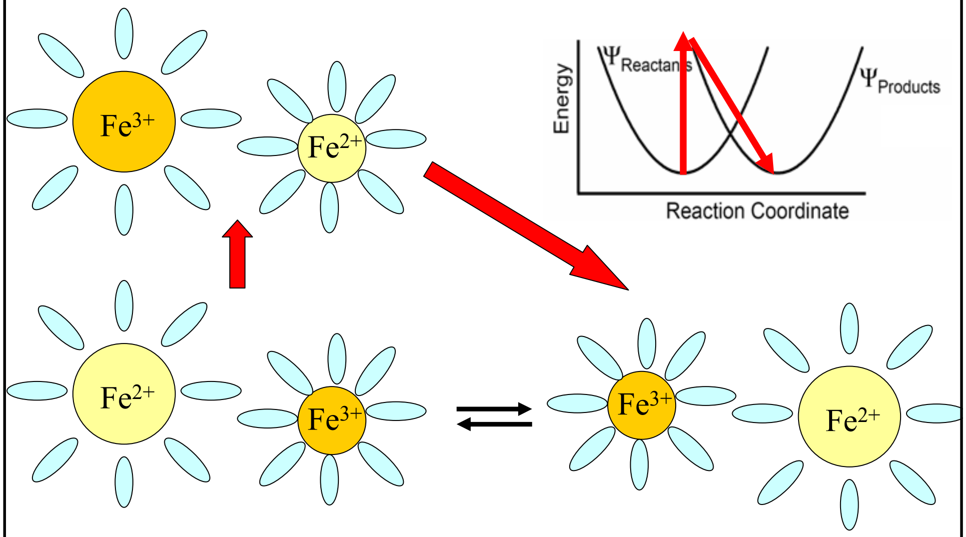
($\Delta G^o = 0$)

$$\mathbf{Fe^{2+} + Fe^{3+} \rightleftharpoons Fe^{3+} + Fe^{2+}}$$

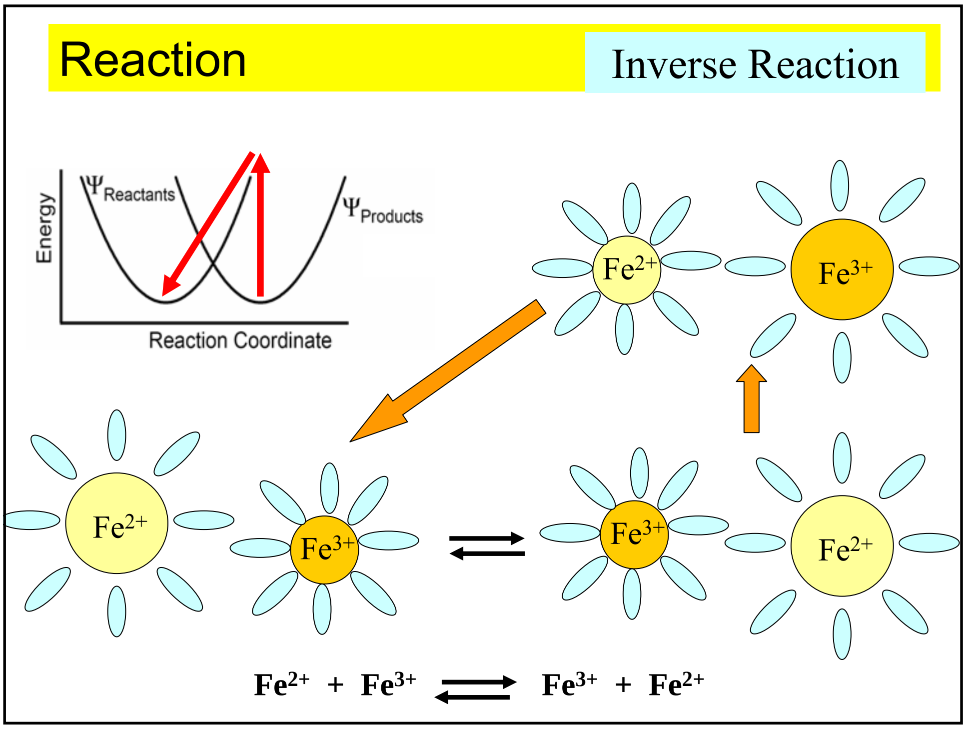


Reaction

Forward Reaction



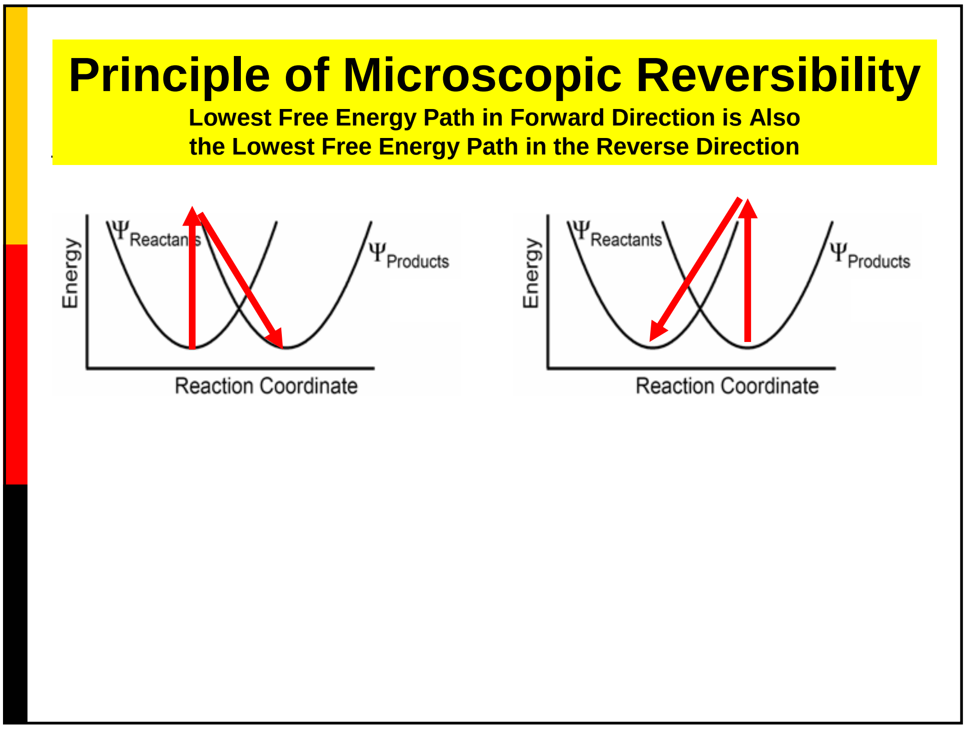
$$\mathbf{Fe^{2+} + Fe^{3+} \rightleftharpoons Fe^{3+} + Fe^{2+}}$$



Reaction

Inverse Reaction

$Fe^{2+} + Fe^{3+} \rightleftharpoons Fe^{3+} + Fe^{2+}$

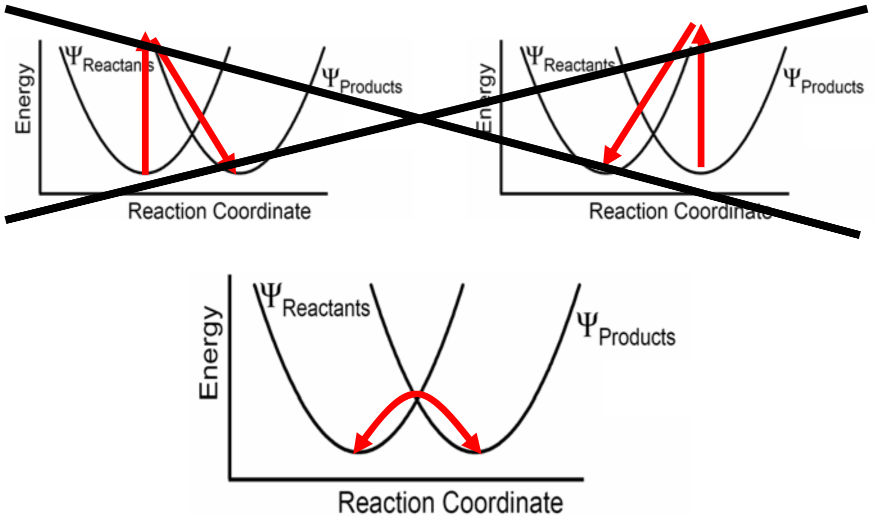


Principle of Microscopic Reversibility

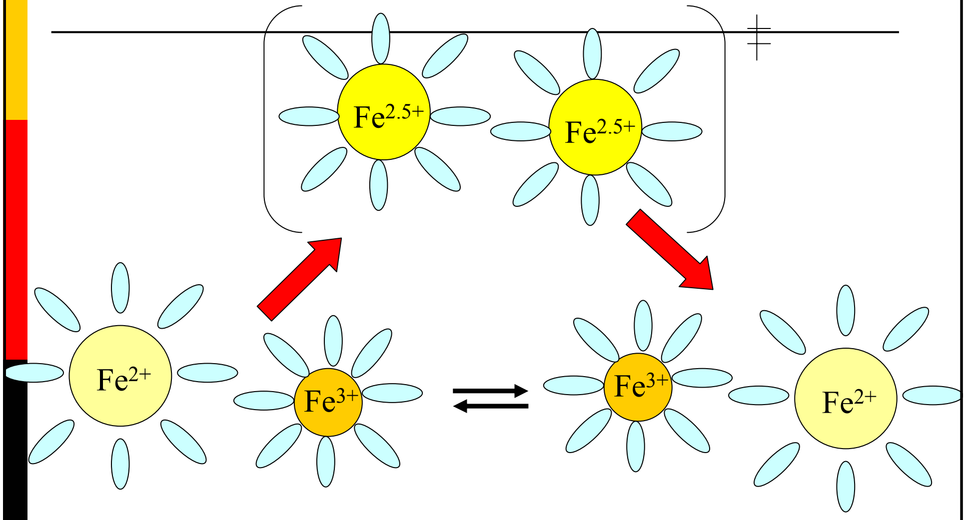
Lowest Free Energy Path in Forward Direction is Also
the Lowest Free Energy Path in the Reverse Direction

Principle of Microscopic Reversibility

Lowest Free Energy Path in Forward Direction is Also the Lowest Free Energy Path in the Reverse Direction



Reaction Profile that obeys the Hammond Postulate and Microscopic Reversibility!



$$Fe^{2+} + Fe^{3+} \rightleftarrows Fe^{3+} + Fe^{2+}$$

Marcus Theory of Electron Transfer

Electron Transfer in a Donor-Acceptor Pair DA:

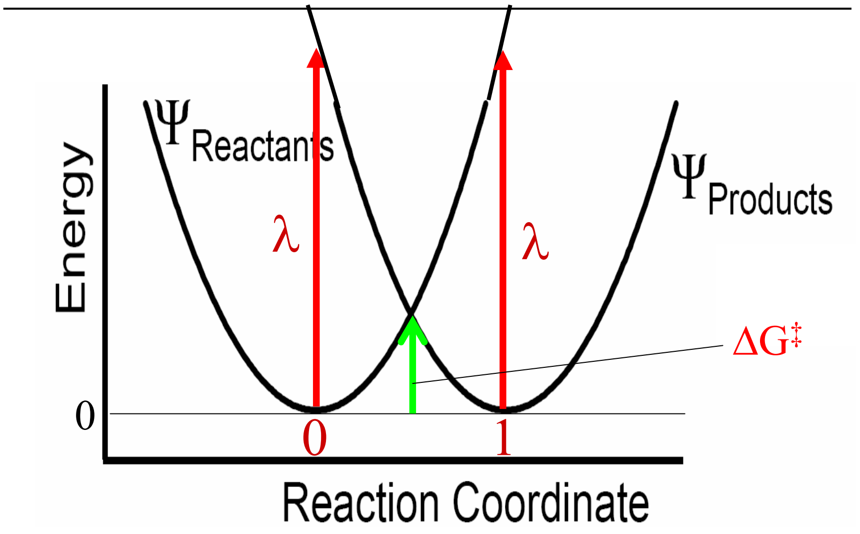
$$DA \rightarrow D^+A^-$$

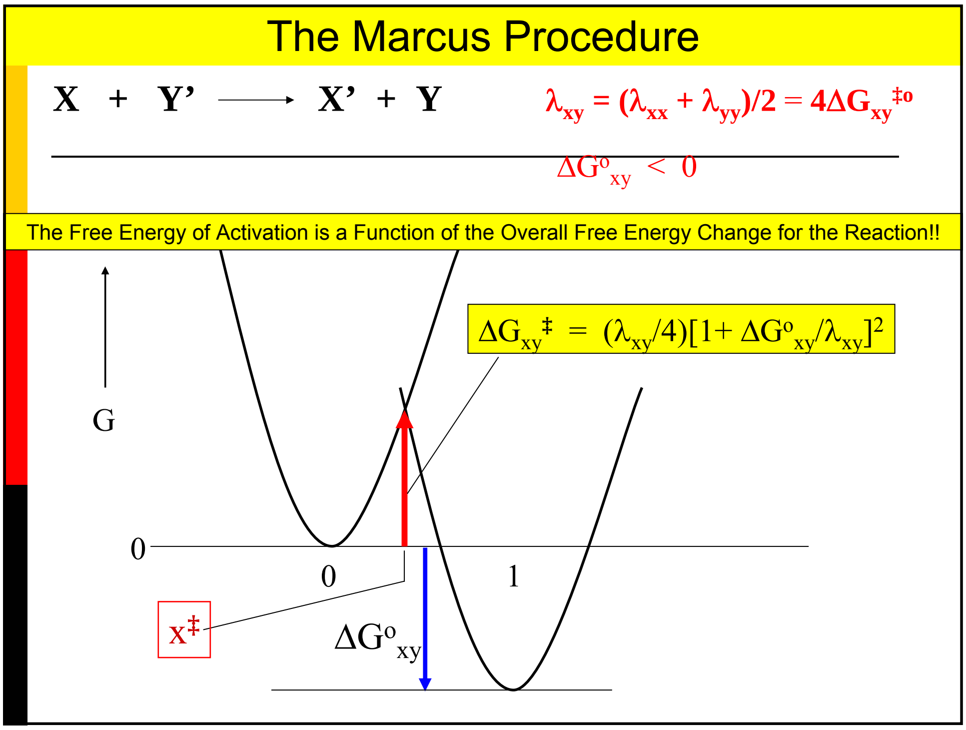
The rate of electron transfer in DA depends on:

The standard Gibbs free energy change of the reaction;

The energy associated with molecular rearrangements (reorganization of solvation shell and ligands).

The (Solvent/Ligand) Reorganization Free Energy (λ)





The Marcus Procedure

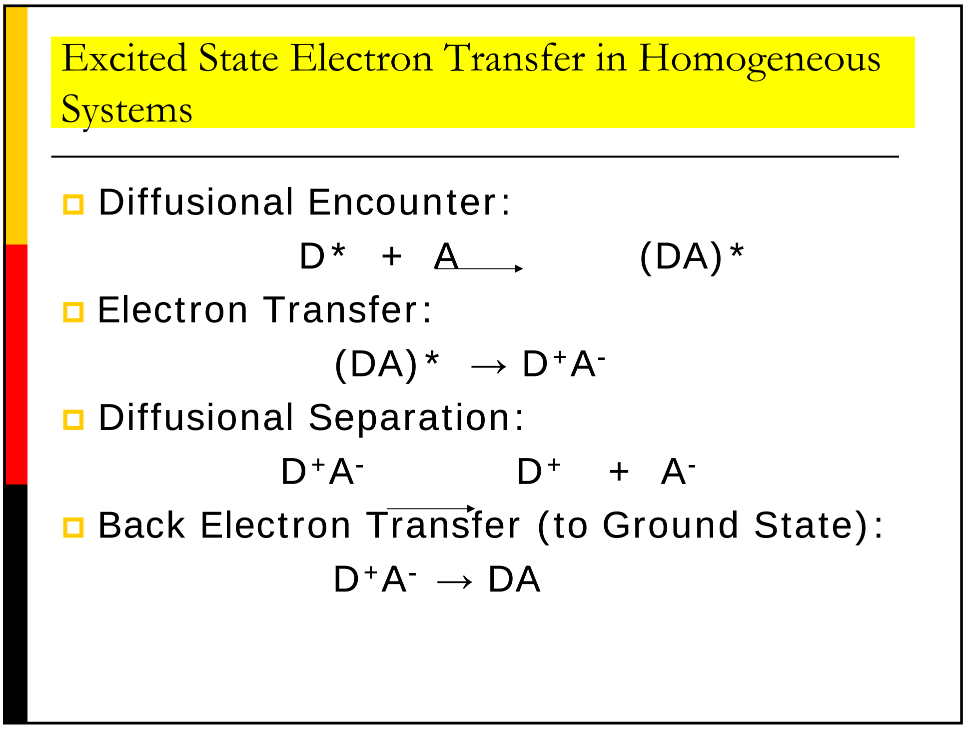
$$X + Y' \longrightarrow X' + Y$$

$$\lambda_{xy} = (\lambda_{xx} + \lambda_{yy})/2 = 4\Delta G_{xy}^{\ddagger o}$$

$$\Delta G^o_{xy} < 0$$

The Free Energy of Activation is a Function of the Overall Free Energy Change for the Reaction!!

$$\Delta G_{xy}^{\ddagger} = (\lambda_{xy}/4)[1 + \Delta G^o_{xy}/\lambda_{xy}]^2$$



Excited State Electron Transfer in Homogeneous Systems

- Diffusional Encounter:

  $D^* + A \longrightarrow (DA)^*$
- Electron Transfer:

  $(DA)^* \rightarrow D^+A^-$
- Diffusional Separation:

  $D^+A^- \longrightarrow D^+ + A^-$
- Back Electron Transfer (to Ground State):

  $D^+A^- \rightarrow DA$

Excited State Electron Transfer in Homogeneous Systems

Electrochemiluminescence

- Diffusional Encounter:

$$D^* + A \rightleftharpoons (DA)^*$$

- Electron Transfer:

$$(DA)^* \rightleftharpoons D^+A^-$$

- Diffusional Separation:

$$D^+A^- \rightleftharpoons D^+ + A^-$$

Excited State Electron Transfer in Homogeneous Systems

Rehm – Weller Kinetic Model

Diffusional Encounter:

$$D^* + A \rightleftharpoons (DA)^* \qquad k_{dif} / k_{-dif}$$

Electron Transfer:

$$(DA)^* \rightleftharpoons D^+A^- \qquad k_{et} / k_{-et}$$

Diffusional Separation:

$$D^+A^- \longrightarrow D^+ + A^- \qquad k_{sep}$$

$$k_q = \frac{k_{dif}}{[1 + (\underset{\Uparrow}{k_{-dif}/k_{et}}) + (k_{-dif}/k_{sep})(\underset{\Uparrow}{k_{-et}/k_{et}})]}$$

Excited State Electron Transfer in Homogeneous Systems

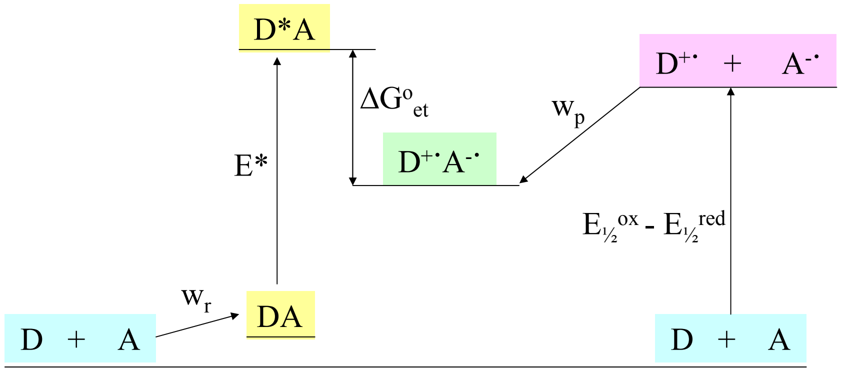
Rehm – Weller Kinetic Model

$$k_q = \frac{k_{dif}}{[1 + \underbrace{(k_{-dif}/k_{et})}_{A\exp(\Delta G^{\ddagger}_{et}/RT)} + (k_{-dif}/k_{sep})\underbrace{(k_{-et}/k_{et})}_{\exp(\Delta G^{o}_{et}/RT)}]}$$

In Acetonitrile:

$$k_q = \frac{2 \times 10^{10}\ M^{-1}s^{-1}}{\{1 + 0.25\,[\exp(\Delta G^{\ddagger}_{et}/RT) + \exp(\Delta G^{o}_{et}/RT)]\}}$$

Calculating the Free Energy Change for Electron Transfer



$$\Delta G^o_{et} = 23.06(E_{1/2}^{ox} - E_{1/2}^{red}) - E^* + (w_p - w_r)$$

Excited State Electron Transfer in Homogeneous Systems

Rehm – Weller Kinetic Model

$$k_q = \frac{k_{dif}}{[1 + \underbrace{(k_{-dif}/k_{et})}_{A\ \exp(\Delta G^{\ddagger}_{et}/RT)} + (k_{-dif}/k_{sep})\underbrace{(k_{-et}/k_{et})}_{\exp(\Delta G^{o}_{et}/RT)}]}$$

In Acetonitrile:

$$k_q = \frac{2 \times 10^{10}\ M^{-1}s^{-1}}{\{1 + 0.25\ [\exp(\Delta G^{\ddagger}_{et}/RT) + \exp(\Delta G^{o}_{et}/RT)]\}}$$

Dynamics of electron transfer

The rate of electron transfer depends on:

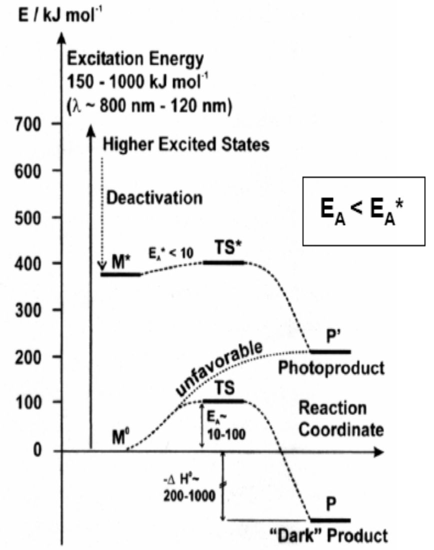
(1) the distance between the electron donor and acceptor;

(2) standard Gibbs free energy change of the reaction;

(3) the energy associated with molecular rearrangements.

Excited State Redox Potentials and Rate Constants for Outer Sphere Electron Transfer in Solution can be Estimated via the Rehm-Weller Model when the Appropriate Redox Parameters are Available or can be Estimated.

Reações Fotoquímicas



Após absorção de um fóton, uma molécula no ES contém excesso de energia, o que torna termodinamicante favorável sua conversão a produtos cuja formação térmica poderia ser energeticamente desfavorável. Devido à competição com os demais mecanismos de desativação, uma reação fotoquímica ocorre a partir do ES de menor energia, S_1 ou T_1, cuja vida útil é suficientemente longa.

Reações Fotoquímicas

$$R \longrightarrow R^*$$
$$R^* \longrightarrow \text{Produto(s)}$$

a) Reação Fotoquímica

$$R \longrightarrow R^*$$
$$R^* \longrightarrow I$$
$$I + Y \longrightarrow \text{Produto(s)}$$

b) Reação Foto-iniciada

Reações Fotoquímicas

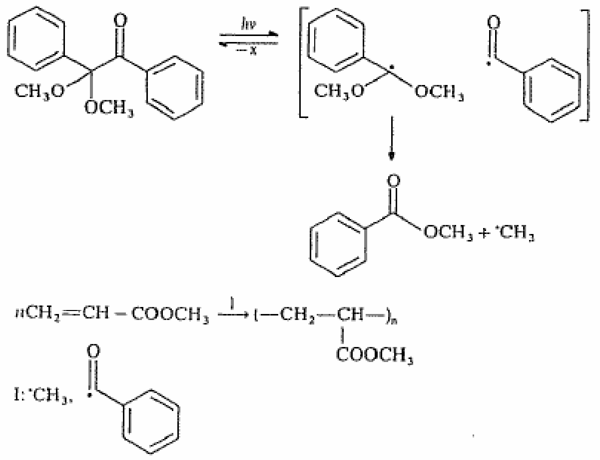


Figure 1.18 Polymerization of *methyl acrylate* photoinitiated by *benzil dimethylacetal* [28]