

Photochemistry II

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PHOTOCHEMISTRY II

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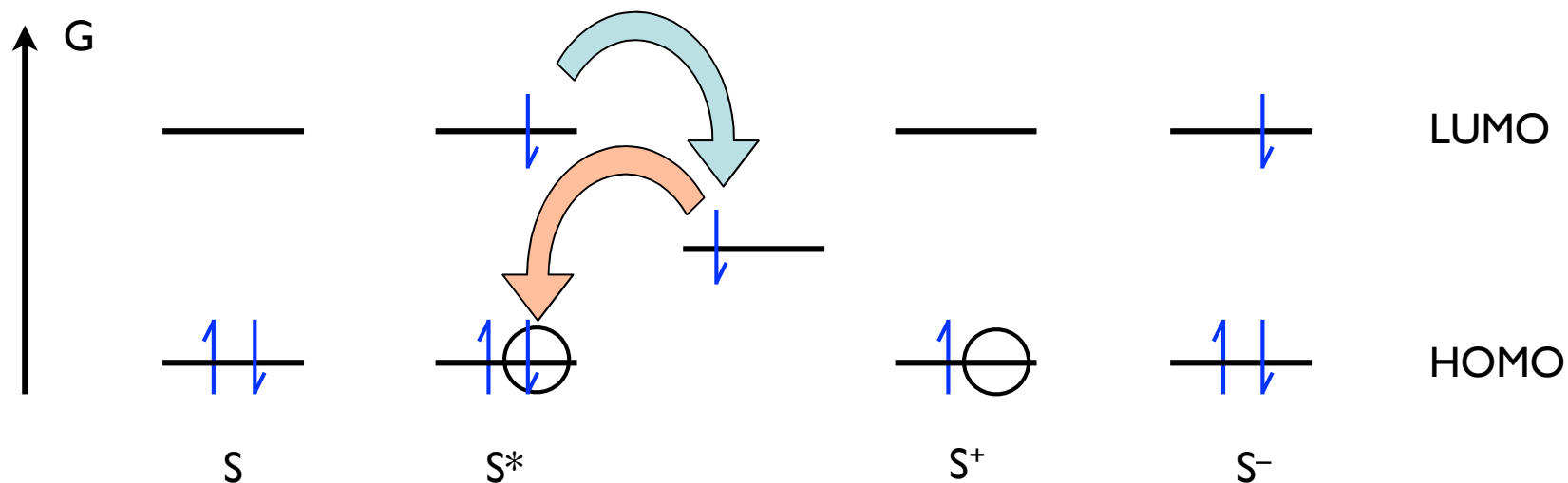
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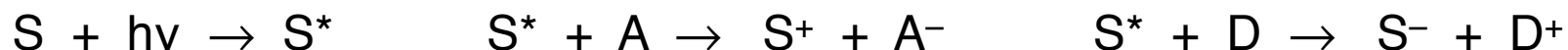
7. Principle of photoinduced electron transfer

7.1 Redox properties of excited states

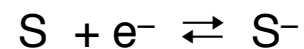
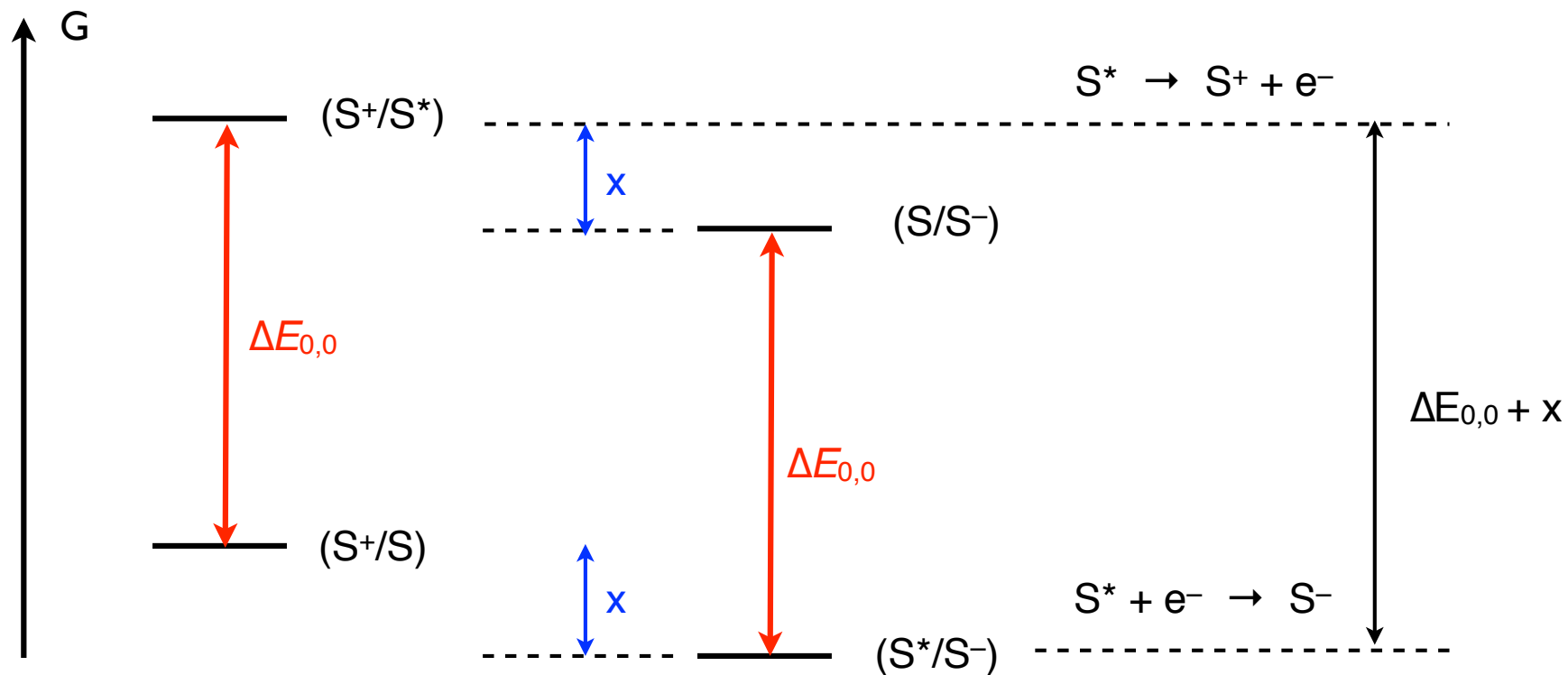


Electronic excited states (S^*) are characterized by redox properties that are quite different from those of the corresponding ground states (S). The electron promoted during the light absorption process to the LUMO and the vacant “hole” left in the HOMO confer the excited state (S^*) reductive AND oxidative properties, respectively.

In the S^* species, the electron in the LUMO is more prone to be transferred to an acceptor orbital at a lower energy level than electrons in the ground state. As well, S^* will accept more easily an electron from a donor species than the ground state.



7.2 Thermodynamics of photoredox reactions



$$\Delta E_{0,0}$$

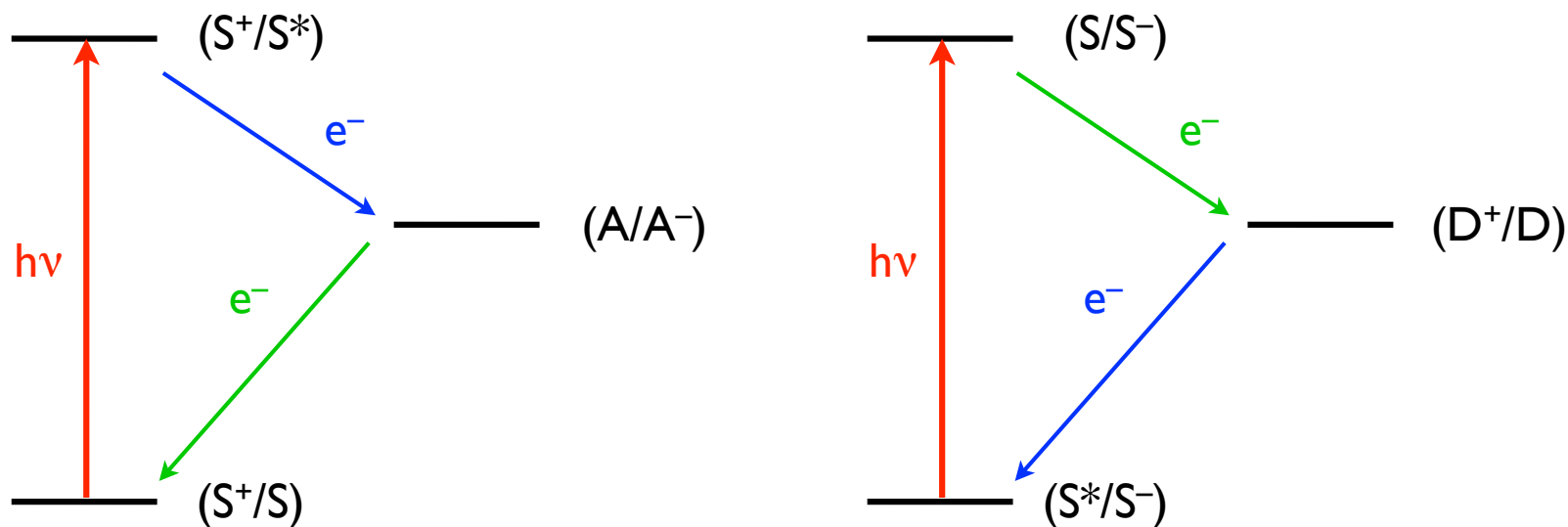
$$\phi^\circ (S^+/S)$$

$$\phi^\circ (S^+/S^*) = \phi(S^+/S) - \Delta E_{0,0} / \mathcal{F}$$

$$\phi^\circ (S/S^-)$$

$$\phi^\circ (S^*/S^-) = \phi(S/S^-) + \Delta E_{0,0} / \mathcal{F}$$

Charge separation and back electron transfer



forward electron transfer



back electron transfer



charge separation



Geminate ion pairs $[S^+ \dots A^-]$ and $[S^- \dots D^+]$ can be separated by solvation of ions in a polar solvent, before recombination takes place. Such a polar medium is therefore a condition for the photoredox reaction to yield products.

Exercise 7.1

A cyanin dye S ($\Delta E_{0,0} = 2.4$ eV) is used as a polymerization initiator in the presence of N-phenylglycin (NPG) and of an acceptor compound (MCP⁺).

List all light-induced electron transfer reactions that can take place between the electronic excited state of the cyanin dye S* and the other reactants.

Write the back electron transfer reactions that are likely to take place later in the dark.

Indicate for each reaction the value of the associated standard free energy $\Delta_r G^0$ [eV].

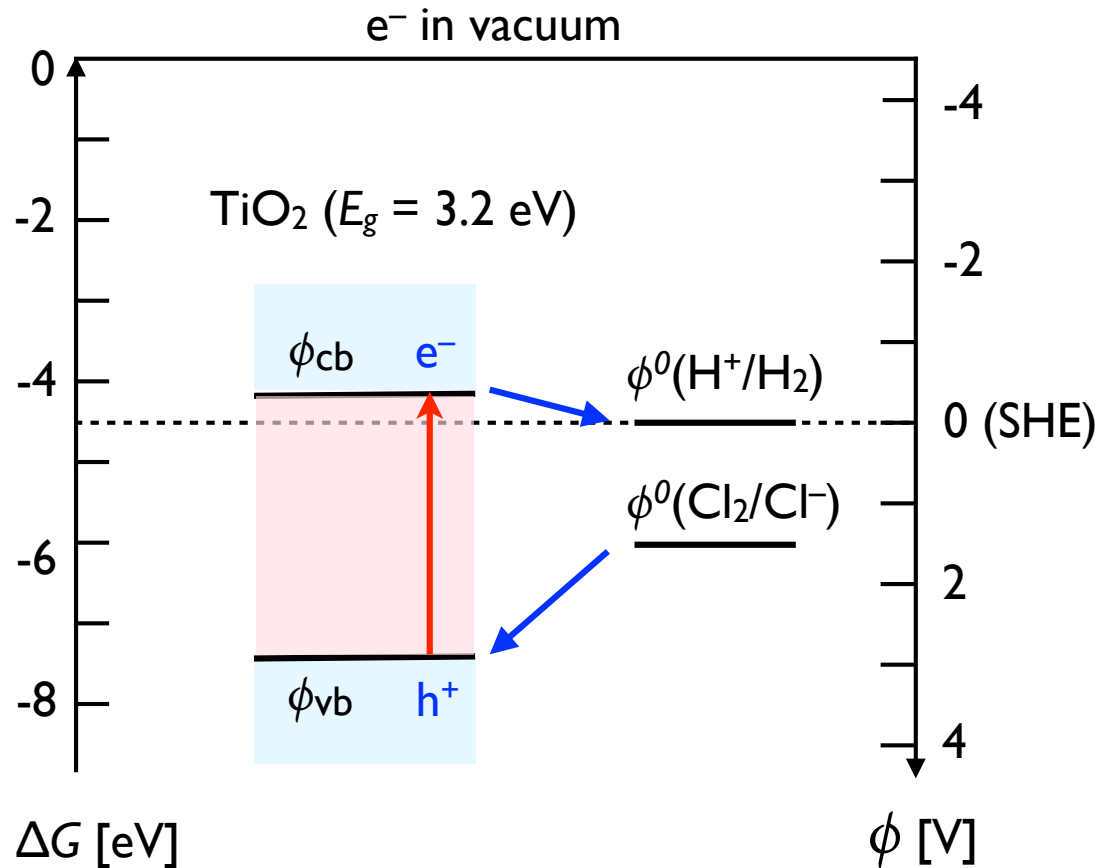
Numerical data

$$\phi^0 (S^+ / S) = + 1.63 \text{ V / SCE}$$

$$\phi^0 (\text{NPG}^+ / \text{NPG}) = + 0.25 \text{ V / SCE}$$

$$\phi^0 (\text{MCP}^+ / \text{MCP}) = - 0.65 \text{ V / SCE.}$$

Photoinduced electron transfer at the surface of semiconductors



The electrochemical potential ϕ of a solid is given by the Fermi level: $\phi = E_F / F$. Under illumination, electrons are out of equilibrium and two quasi Fermi levels have to be considered for negative (n) and positive (p), charge carriers, respectively:

$$E_{F,n}^* = E_C + kT \cdot \ln \frac{n^*}{N_C}$$

$$E_{F,p}^* = E_V - kT \cdot \ln \frac{p^*}{N_V}$$

where E_C and E_V are the conduction and valence band

edge energies, N_C and N_V the effective density of states in the bands, and n^* and p^* the out-of-equilibrium concentrations of both carriers.

Photoinduced electron transfer at the surface of semiconductors

In semiconductors containing a concentration N_d of donor impurities (n-doping), or N_a of acceptor impurities (p-doping), one has at the equilibrium:

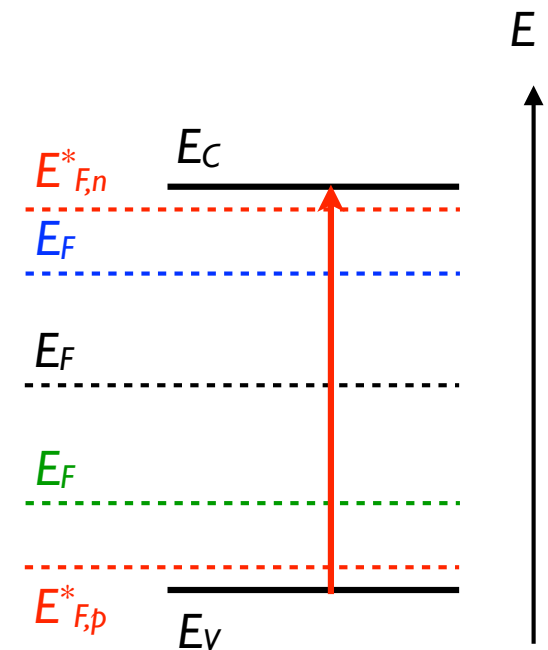
$$E_F = E_C + kT \cdot \ln \frac{N_d}{N_C}$$

$$E_F = E_V - kT \cdot \ln \frac{N_a}{N_V}$$

Under illumination, quasi-Fermi level expressions become:

$$E_{F,n}^* = E_C + kT \cdot \ln \frac{N_d + n^*}{N_C} \approx E_C$$

$$E_{F,p}^* = E_V - kT \cdot \ln \frac{N_a + p^*}{N_V} \approx E_V$$



intrinsic semiconductor

n-doped p-doped

under illumination

Exercise 7.2

a) A carboxylated derivative of methyl-viologen (CMV^-) is strongly adsorbed on the surface of TiO_2 colloidal particles dispersed in an acidic aqueous solution ($\text{pH} = 1$). The semiconducting oxide is characterized by numerous oxygen vacancies that imply a strong n-doping of the material.

Write all photoredox reaction that are expected to take place upon UV irradiation of the system.

Estimate for all processes the value of associated standard free energy $\Delta_r G^0$ [eV].

b) Repeat the problem for the same acceptor compound adsorbed on the surface of intrinsic (undoped) TiO_2 particles under low intensity UV irradiation, knowing that in the steady irradiation state, the concentration of out-of-equilibrium charge carriers is 10^{17} cm^{-3} .

Numerical data

$$\phi^0 (\text{CMV}^- / \text{CMV}^{2-}) = + 0.04 \text{ V} / \text{SHE}$$

$$\phi_{cb} (\text{TiO}_2, \text{pH} = 1) = - 0.12 \text{ V/NHE}$$

$$E_g (\text{TiO}_2) = 3.2 \text{ eV}$$

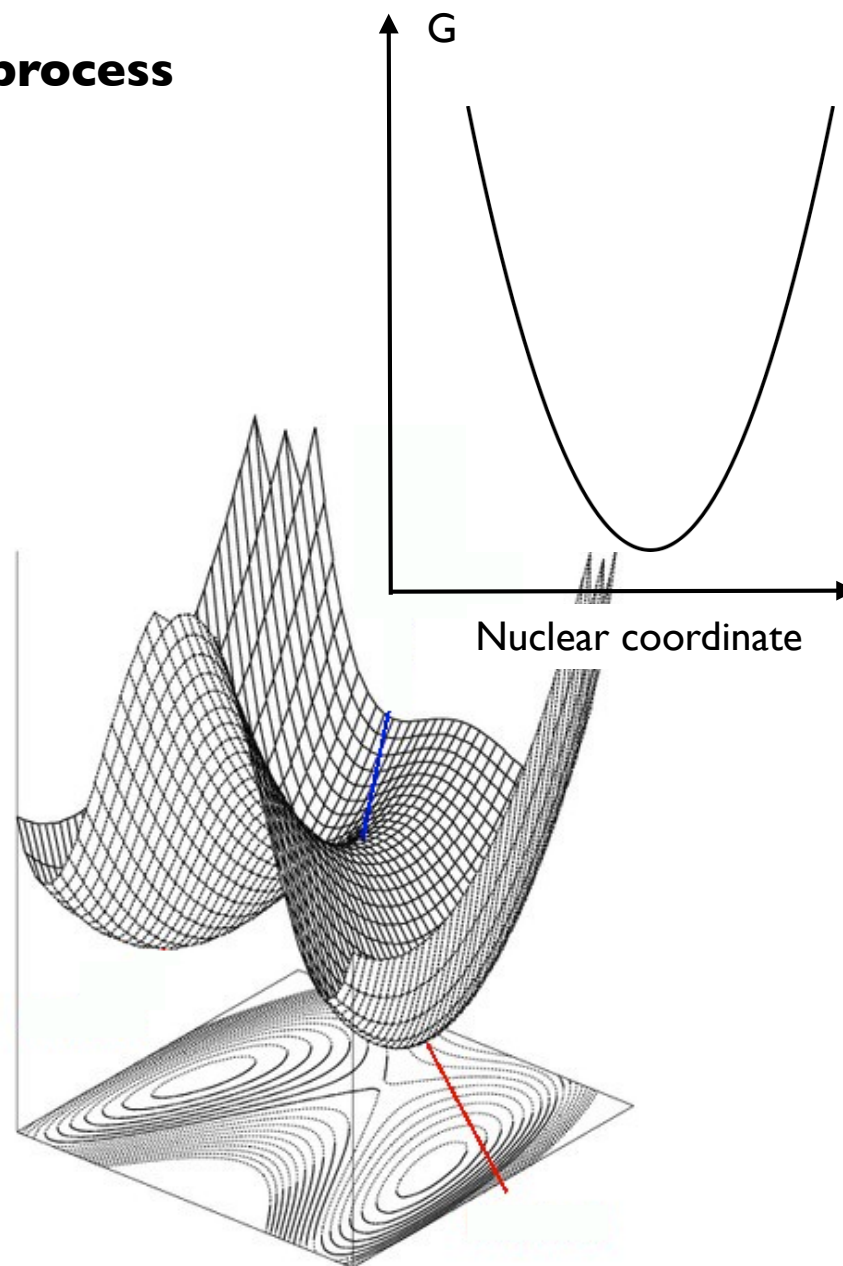
$$N_V = N_C (\text{TiO}_2) = 10^{21} \text{ cm}^{-3} .$$

7.3 Dynamics of ET reactions

Vibration-mediated electron transfer process

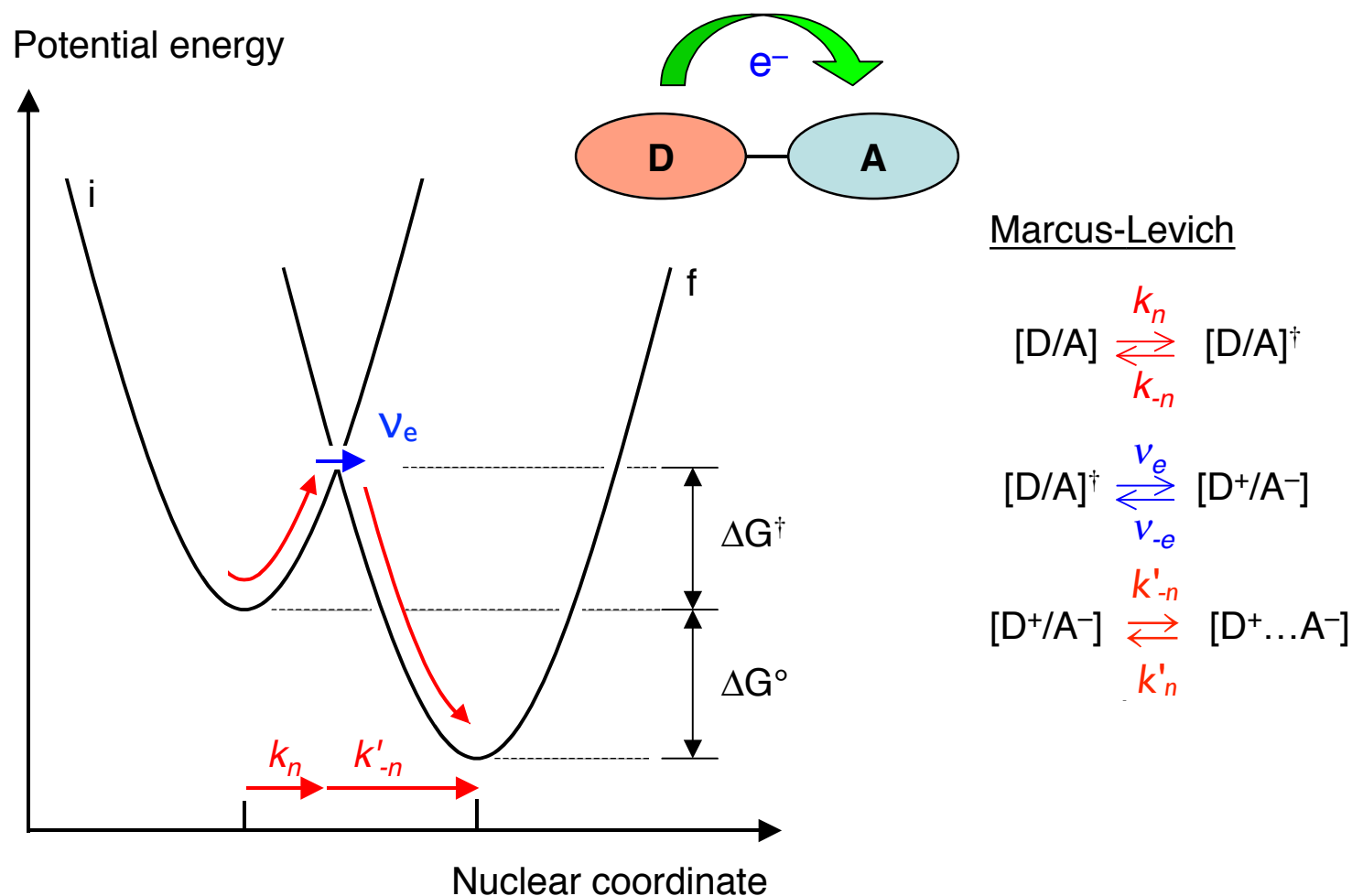
In the case of a harmonic oscillator, the relation between energy and bond length gives a parabolic potential curve (Hooke's law), and provides the framework for discussion of the dependence of energy on vibrational state.

This description is useful in discussion of the energy levels in more complicated systems. The distance is replaced by a **nuclear coordinate**, which lumps together all the distances in all the bonds, all angle changes, and even the configuration of surrounding solvent dipoles, in a single representative parabola. This is obviously a gross simplification (the real picture would require a multidimensional representation), but it provides a handy frame of reference.



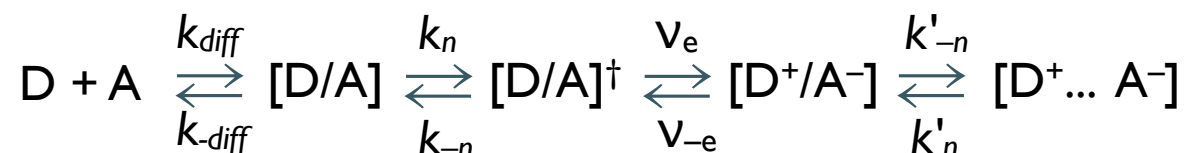
Nuclear reorganization-controlled ET kinetics

The electron transfer step takes place according to the Franck-Condon principle: The rate of the overall electron transfer process from the initial D/A precursor state to the charge-separated successor state ($D^+...A^-$) is limited by the rate of the slower nuclear reorganization (Marcus-Levich).



Dynamics of ET reactions

The kinetics of the overall reaction between an electron donor species D and an acceptor A can be divided into 4 consecutive steps:



- 1) Diffusion of reactive species (k_{diff}), encounter of D and A and formation of a precursor complex $[D/A]$ with a stability constant $K_A = k_{diff} / k_{-diff}$.
- 2) Nuclear reorganization of the precursor complex (k_n) until a configuration $[D/A]^\ddagger$ (activation complex) is reached that allows for electron transfer.
- 3) Electron transfer at the activation complex nuclear coordinate (V_e). The obtained successor complex $[D^+/A^-]$ has the same nuclear configuration.
- 4) Nuclear relaxation of the successor complex and dissociation (k'_{-n}) to a charge-separated geminate pair $[D^+ \dots A^-]$.

Dynamics of ET reactions

In the steady-state approximation of intermediate species:

$$\frac{1}{k_{obs}} = \frac{1}{k_{diff}} + \frac{1}{k_{act}}$$

$$k_{diff}: \text{diffusion rate constant} = \frac{8 k_B T}{3 \eta} \sim 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1} \quad (\eta : \text{viscosity})$$

k_{act} : activation-controlled rate constant for ET

$$\text{If } k_{act} \ll k_{diff}: \quad k_{obs} = k_{act} = \frac{K_A \cdot k_n \cdot k'_{-n} \cdot v_e}{(k_{-n} + k'_n) \cdot v_e + k_{-n} \cdot k'_n}$$

If $k_n = k'_{-n}$ and $k_{-n} = k'_n$, the activated complex is said (kinetically) "symetric".

In this case, the last relationship simplifies to yield:

$$k_{act} = \frac{K_A \cdot k_n \cdot v_e}{2 v_e + k_{-n}} = K_A \cdot \frac{k_n \cdot v_e}{2 v_e + k_{-n}} = K_A \cdot k_{et}$$

Formation of the precursor complex

The rate at which the donor species D will encounter an acceptor A at a distance r is given by Smoluchowski's equation:

$$k_{diff} = \frac{4\pi \cdot r \cdot N_A}{1000} \cdot (D_D + D_A) \text{ [mol}^{-1} \cdot \text{l} \cdot \text{s}^{-1} \text{]} \quad D_D, D_A : \text{diffusion coefficients}$$

The ET process can actually take place over a range of encounter distances. k_{act} is thus obtained by integrating over a distribution of distances r , weighted by the characteristic electron transfer rate $k_{et}(r)$:

$$k_{act} = \int_0^{\infty} \frac{4\pi \cdot r^2 \cdot N_A}{1000} \cdot \exp\left[\frac{-w(r)}{RT}\right] \cdot k_{et}(r) dr$$

$w(r)$ is the electrostatic work necessary to bring electrically charged species D and A from an infinite distance to the reaction distance r . The integral can be factorized to yield:

$$k_{act}(r_m) = K_A(r_m) \cdot k_{et}(r_m) \quad r_m \pm \delta r \text{ represents the distance over which } k_{et} \gg 0.$$

$$K_A(r_m) = \frac{4\pi \cdot N_A \cdot r_m^2 \cdot \delta r}{1000} \cdot \exp\left[\frac{-w(r_m)}{RT}\right] \quad (\text{typically, } \delta r \approx 0.8 \text{ \AA})$$

Nuclear reorganization of the precursor complex

According to the Born-Oppenheimer approximation, v_e is large compared to k_{-n} . The expression of k_{et} then becomes :

$$k_{et} = \frac{k_n \cdot v_e}{2 v_e + k_{-n}} \approx \frac{k_n}{2} = 1/2 K_n \cdot k_{-n}$$

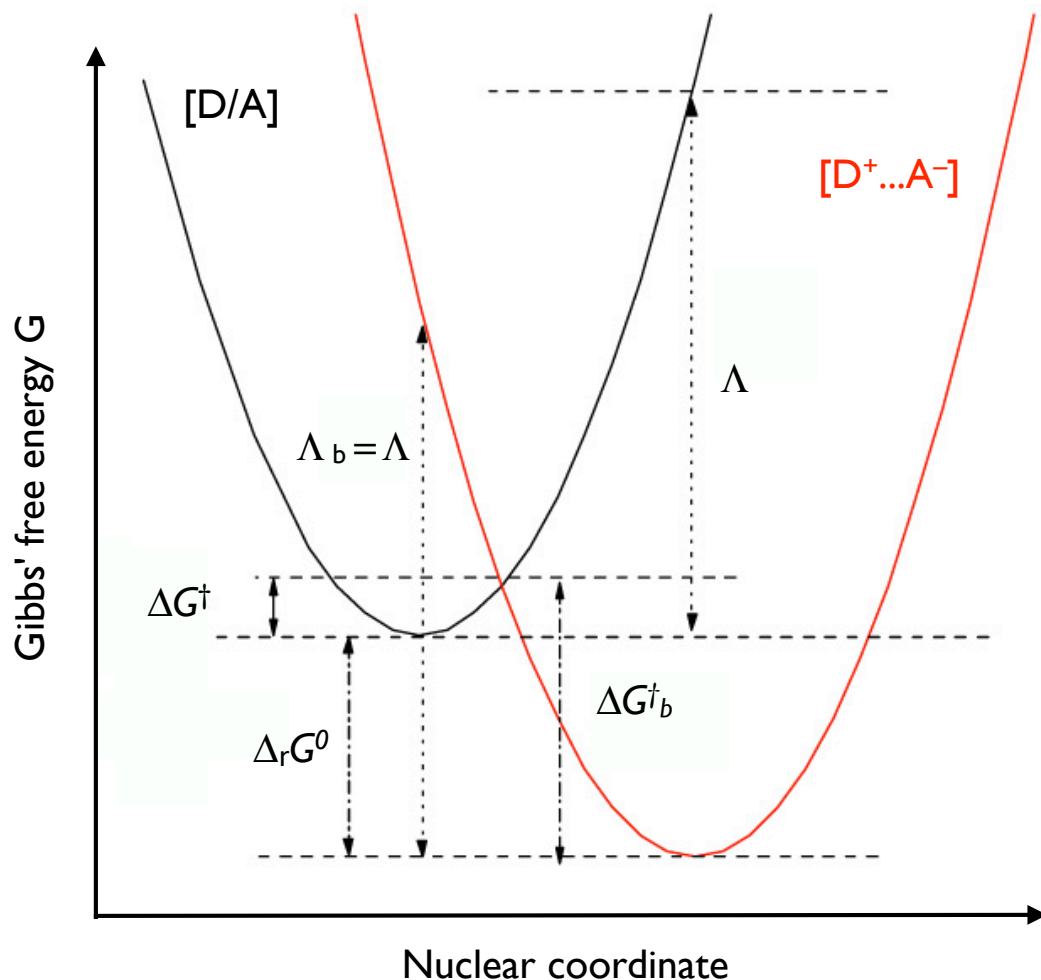
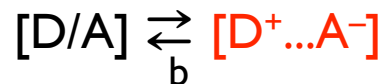
where $K_n = k_n / k_{-n} = \exp(-\Delta G^\ddagger / RT)$

ΔG^\ddagger is the activation free energy of the precursor complex

$$\underline{k_{et} = 1/2 k_{-n} \cdot \exp(-\Delta G^\ddagger / RT)}$$

Within the frame of the various approximations used, the rate of ET transfer depends upon both the dynamics of the nuclear relaxation k_{-n} and the height of the nuclear reorganization activation barrier ΔG^\ddagger .

Nuclear reorganization energy Λ



The reactant initial state $[D/A]$ and the charge-separated final state $[D^+ \dots A^-]$ differ in the location of the transferring electron, in the molecular geometries of the reactant and product molecules/ ions and in the structure and orientation of the surrounding solvent dipoles.

The **reorganization energy** Λ (always > 0) is the free energy necessary to reorganize the precursor state from its equilibrium nuclear coordinate to that of the successor state.