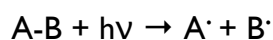


3. Photochemical reactions

3.1 Photodissociation reactions

Types of photochemical reactions

1) Photo-dissociation



2) Photo-induced rearrangements, isomerization



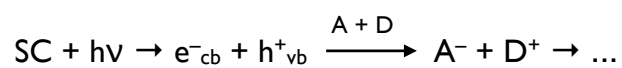
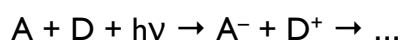
3) Photo-addition



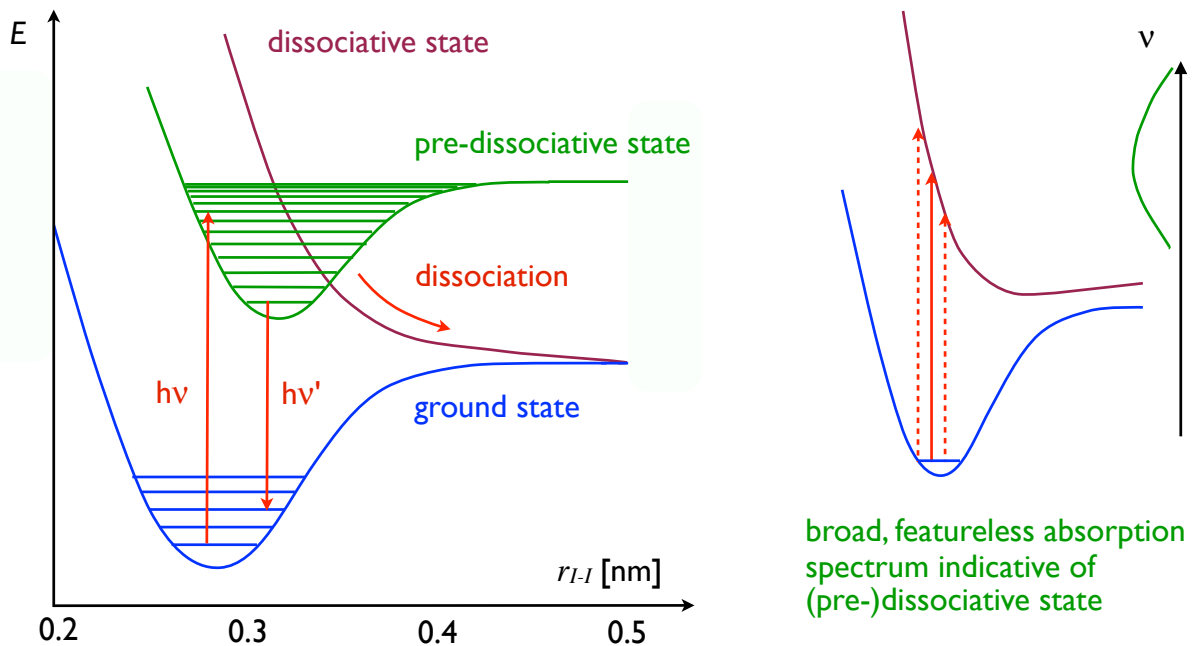
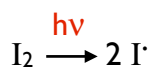
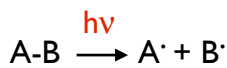
4) Photo-substitution



5) Photo-redox reactions



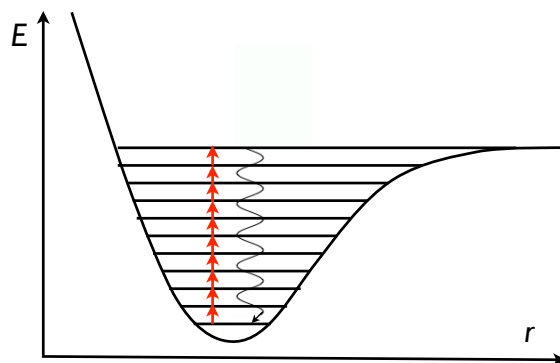
Photodissociation reaction



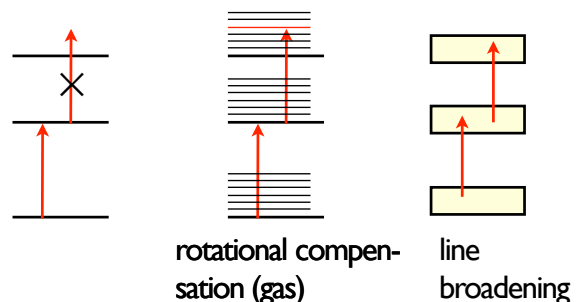
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Photodissociation reaction

Single photons in the IR spectral range are not energetic enough for direct photodissociation of molecules. However, after absorption of multiple infrared photons a molecule may gain internal energy to overcome its barrier for dissociation. Multiple photon dissociation (MPD) can be achieved by applying high power lasers, e.g. a CO₂ laser or a free-electron laser, or by long interaction times of the molecule with the radiation field without the possibility for rapid cooling, e.g. by collisions. The latter method allows even for MPD induced by black body radiation. Main application of this phenomenon is in isotope separation (CF₂DCI, ²³⁵UF₆, ¹³C...)



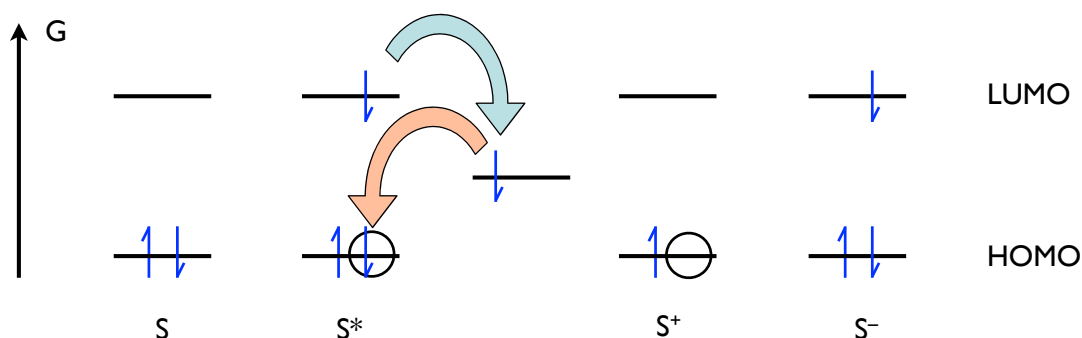
Overcoming the anharmonicity barrier:



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3.1 Light-induced electron transfer

Photoredox (electron transfer) reactions



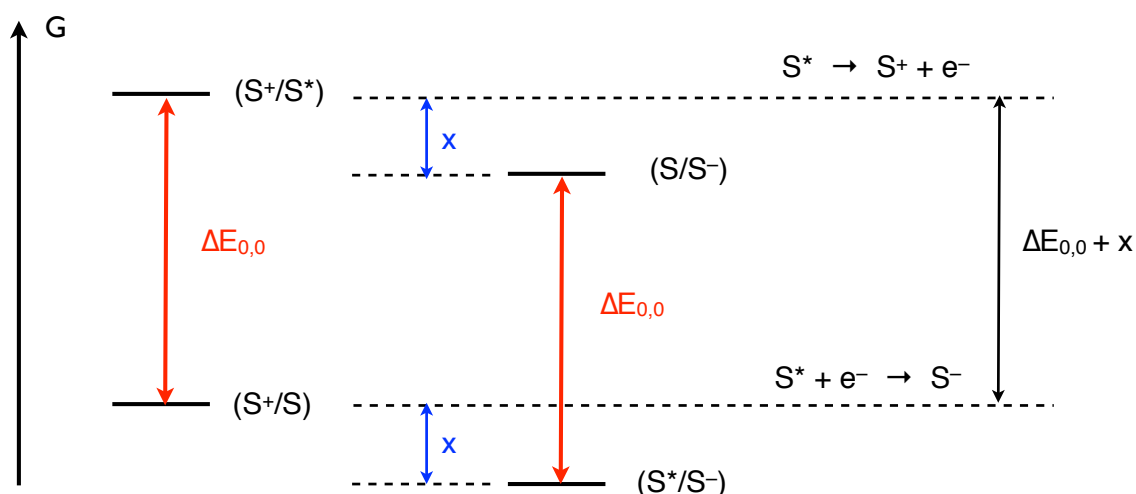
Electronic excited states (S^*) are characterized by redox properties that are quite different from those of the corresponding ground states (S). The electron promoted during the light absorption process to the LUMO and the vacant “hole” left in the HOMO confer the excited state (S^*) reductive AND oxidative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



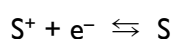
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Thermodynamics of photoredox reactions



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

$$\Delta G [\text{eV}] = -n \mathcal{F} \cdot \phi [\text{V}]$$



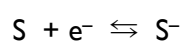
$$\phi^\circ (S^+/S)$$

$$\mathcal{F} = 1 \text{ eV} \cdot \text{V}^{-1}$$



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

Faraday's constant



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



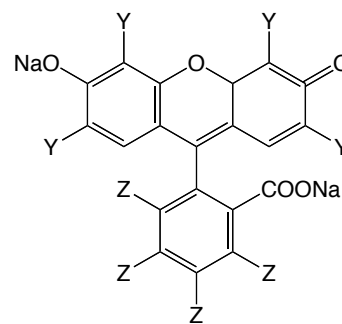
$$\phi^\circ (S^*/S^-) = \phi^\circ (S/S^-) + \Delta E_{0,0} / \mathcal{F}$$

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Thermodynamics of photoredox reactions

It was found experimentally (Loutfy & Sharp, 1976) that a same value of the potential difference $x = \phi^0(S/S^-) - \phi^0(S^+/S^*) = \phi^0(S^*/S^-) - \phi^0(S^+/S) = 0.35 \text{ V}$ is common for a number of organic dyes characterized by a flat aromatic structure .

A simple relation then exists between the oxidation and reduction potentials of the dye, which allows to predict all energy levels of a given photoredox system from the measured values of $\phi^0(S^+/S)$ and $\Delta E_{0,0}$.

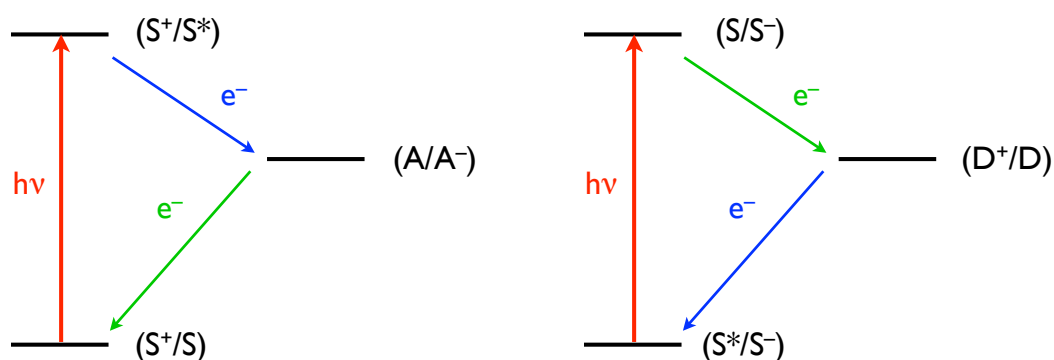


xanthene dyes

Dye	Y	Z	$\Delta E_{0,0}$ [eV]	$\phi^0(S/S^-)$ [V]	$\phi^0(S^+/S)$ [V]	x [V]
rose bengal	-I	Cl	2.20	-1.13	0.72	0.35
erythrosin	-I	-H	2.31	-1.10	0.86	0.35
eosin	-Br	-H	2.33	-1.09	0.89	0.35
fluorescein	-H	-H	2.52	-1.25	0.91	0.36

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Charge separation and electron back transfer



forward electron transfer



back electron transfer



charge separation

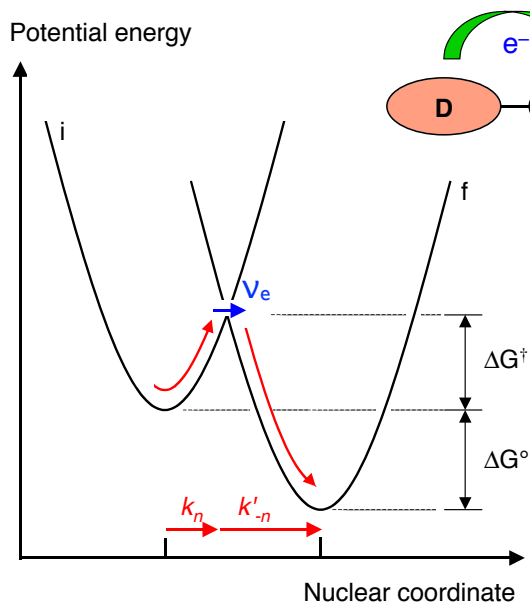


Geminate ion pairs $[S^+ \dots A^-]$ and $[S^- \dots D^+]$ can be separated by solvation of ions in a polar solvent, before recombination takes place. Such a polar medium is therefore a condition for the photoredox reaction to yield products.

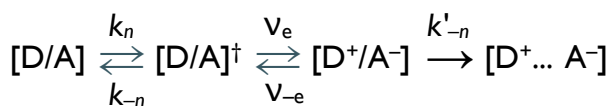
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Vibration-mediated electron transfer (ET)

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



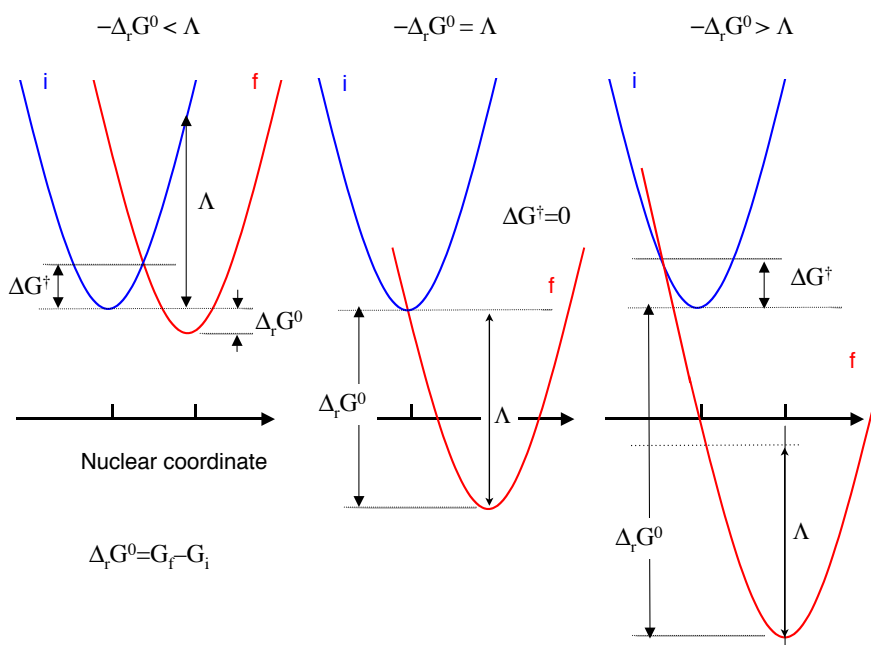
The electron transfer itself can be seen as occurring according to the Franck-Condon principle. The rate of the overall electron transfer process from the initial D/A precursor state to the charge-separated successor state (D⁺...A⁻), therefore, is limited by the rate of the slower nuclear reorganization (Marcus-Levich).



$$k_{et} = \frac{k_n V_e}{2 V_e + k_{-n}}$$

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Activation energy (ΔG^\ddagger) dependence upon exoergicity ($\Delta_r G^0$) of ET



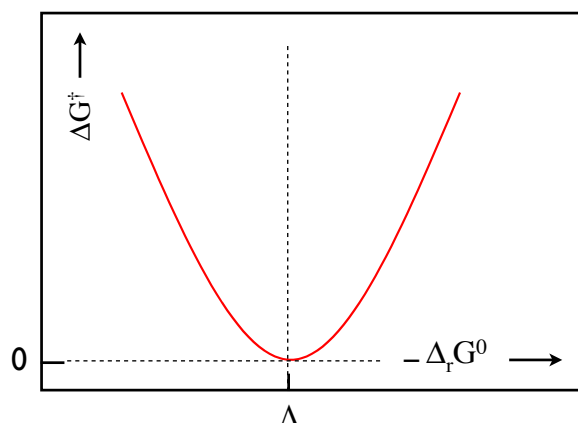
The reorganization energy Λ (always >0) is the free energy necessary to reorganize the precursor state from its equilibrium nuclear configuration to that of the successor state.

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Dynamics of electron transfer processes

Marcus developed an original theory to explain the rate of ET reactions (1956), linking the thermodynamics of the process to its kinetics. A simple quadratic relation between the free energy of the ET reaction $\Delta_{et}G^0$ and the activation energy ΔG^\ddagger was derived :

$$\Delta G^\ddagger = \frac{(\Lambda + \Delta_r G^0)^2}{4\Lambda}$$



Rudolph A. Marcus
(1923-)
Nobel prize 1992

This result was obtained with the assumptions that a) both precursor and successor states are described by parabolic potential curves of similar widths, b) nuclear reorganization proceeds *classically* through low frequency vibrational and rotational modes, and c) that nuclear reorganization is kinetically "symmetrical" with $k_n = k_{-n}$.

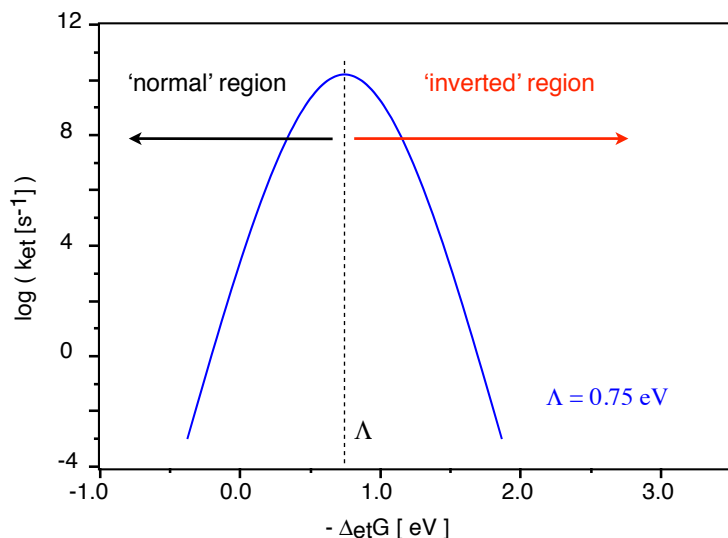
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Dynamics of electron transfer processes

Arrhenius/ Eyring

Marcus

$$k_{et} = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \longrightarrow \ln k_{et} = B - \frac{(\Lambda + \Delta_r G^0)^2}{4\Lambda RT}$$

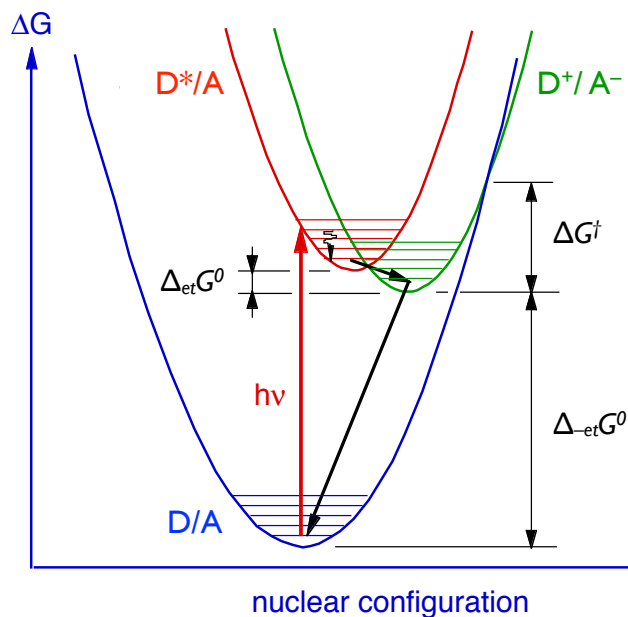


Marcus' quadratic equation predicts some counter-intuitive kinetic behavior as the driving force becomes greater than the reorganization energy ($-\Delta_{et}G^0 > \Lambda$): The theoretical value of the activation energy ΔG^\ddagger starts to raise again, hence reducing the overall ET process rate constant k_{et} .

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

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Dynamics of light-induced electron transfer

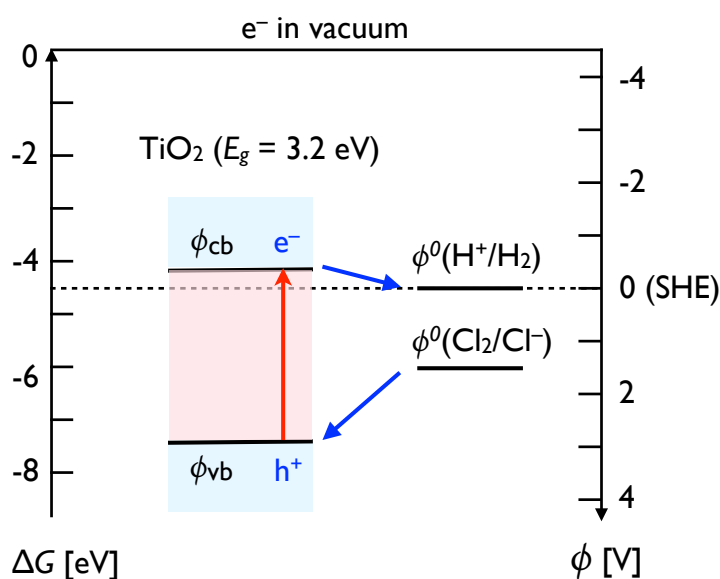


In practical applications of photo-induced ET reactions, charge separation has to be maintained during a period of time sufficient for further redox reactions to take place. Ideally, forward ET involving an excited state has to be as fast as possible, while back electron transfer during which charges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

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

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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.

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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:

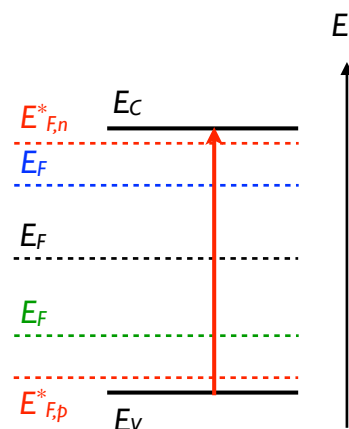
$$E_F = E_C + kT \cdot \ln \frac{N_d}{N_C}$$

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

Under illumination, quasi-Fermi level expressions become:

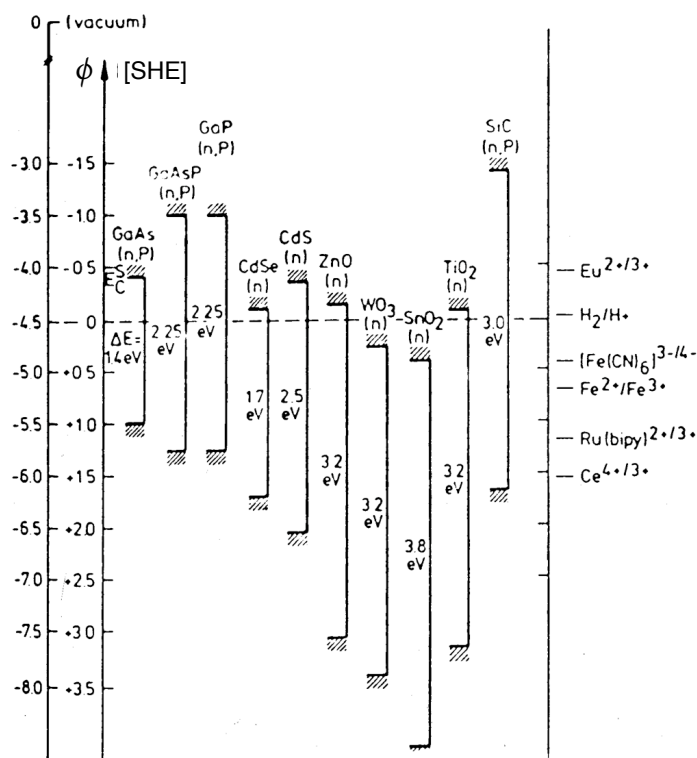
$$E_{F,n}^* = E_C + kT \cdot \ln \frac{N_d + n^*}{N_C} \approx E_C$$

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



intrinsic semiconductor
 n-doped p-doped
 under illumination

Band edge potentials of semiconductors



Values of bandgap energies and of conduction- and valence band edge potentials of various semiconductors are provided here. Because potentials characterizing amphoteric oxides vary with the pH, all values are given for materials in contact with an aqueous solution in standard conditions ($pH = 0.0$).

Wide-bandgap metal oxides are characterized by values of $\phi_V \geq +3.0$ V/SHE. Valence band holes in such semiconductors are thus very strong oxidizing species.

Marcus vs. Tafel equation

In electrochemistry, Butler-Volmer's equation relates the current density j through an electrode to the overpotential η , 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:

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

where k_{et}^0 represents the rate constant of electron transfer in reversible conditions ($\eta = 0$), α is a symmetry- or configuration coefficient and \mathcal{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 $-\Delta_{et}G^0 \ll \Lambda$.

