Electron Transfer

Energy Transfer
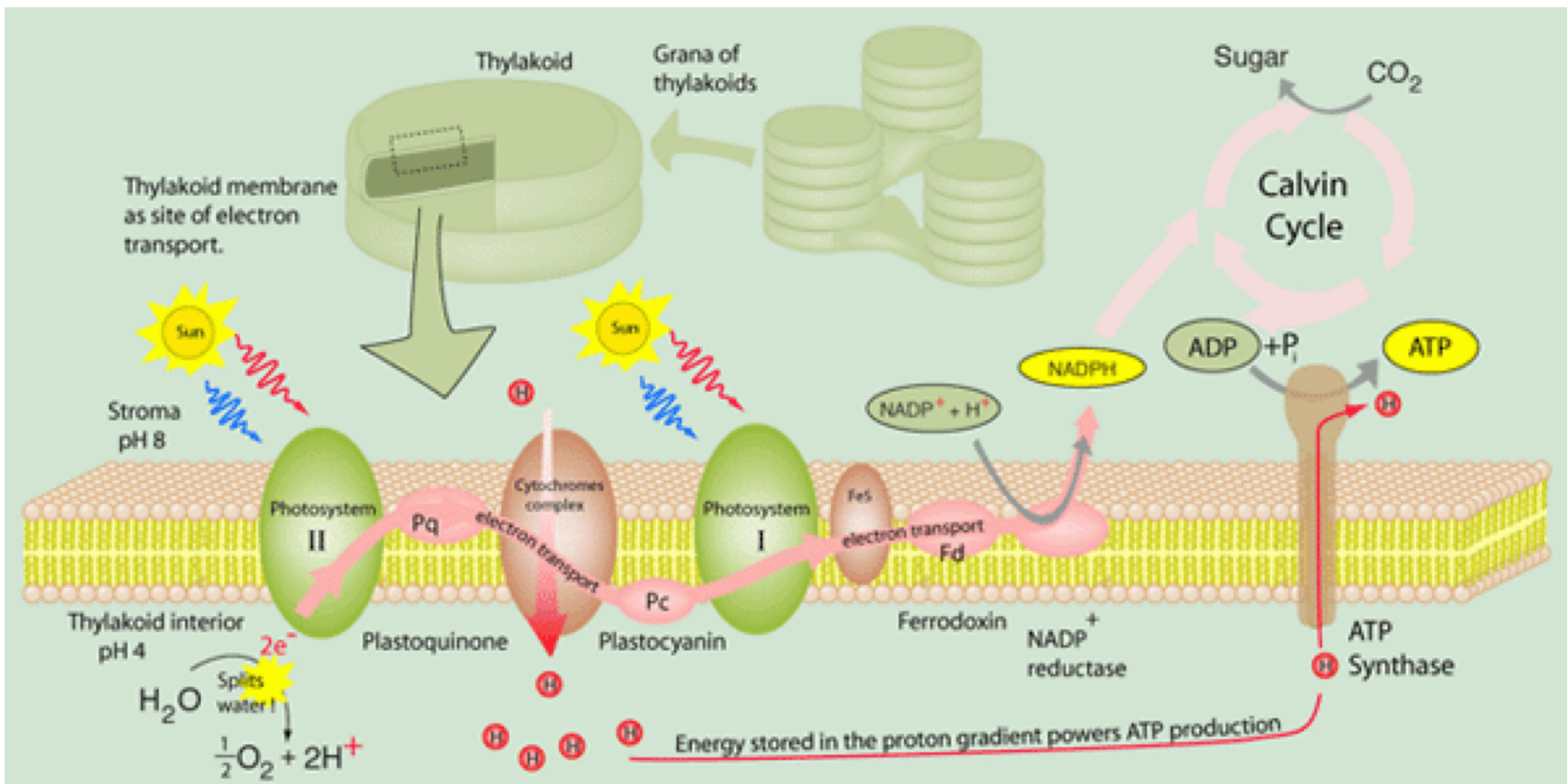
$^1D^* + A \longrightarrow D + {}^1A^*$

$^1D^* + A \longrightarrow D + {}^3A^*$
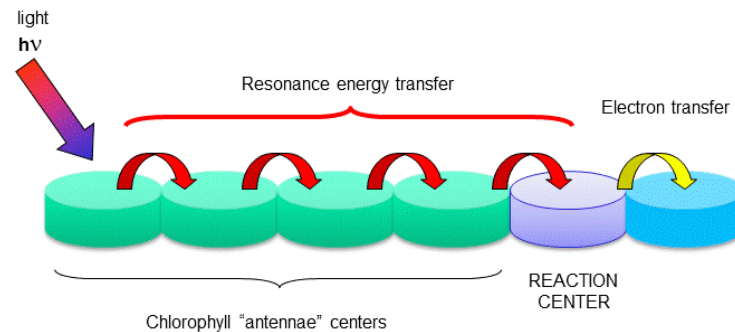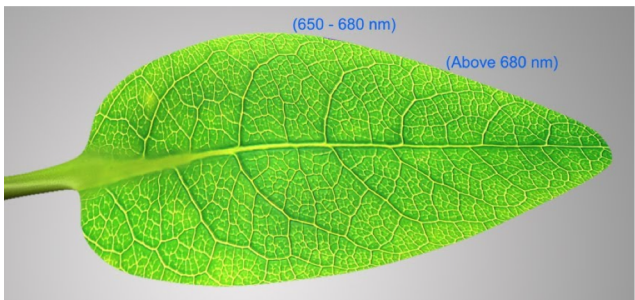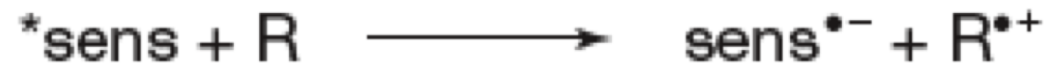
$^3D^* + A \longrightarrow D + {}^1A^*$

$^3D^* + A \longrightarrow D + {}^3A^*$

Survival Strategy: Photosynthesis

(650 - 680 nm)

(Above 680 nm)

light
$h\nu$

Resonance energy transfer

Electron transfer

REACTION CENTER

Chlorophyll "antennae" centers

Thylakoid

Grana of thylakoids

Sugar

CO_2

Calvin Cycle

Thylakoid membrane as site of electron transport.

Sun

Sun

ADP $+P_i$

ATP

NADPH

Stroma pH 8

$NADP^+ + H^+$

H

Cytochromes complex

Photosystem II

Pq

electron transport

Photosystem I

FeS

electron transport

Fd

Thylakoid interior pH 4

$2e^-$

Plastoquinone

Pc

Plastocyanin

Ferrodoxin

$NADP^+$ reductase

ATP Synthase

H_2O

Splits water !

$\frac{1}{2}O_2 + 2H^+$

H H H H

Energy stored in the proton gradient powers ATP production

Electron Transfer

$$sens \xrightarrow{h\nu} {}^*sens$$

$$^*sens + R \longrightarrow sens^{\bullet-} + R^{\bullet+}$$

$$^*sens^{\bullet-} + R^{\bullet+} \longrightarrow R + sens$$

$$R^{\bullet+} \longrightarrow P^{\bullet+}$$
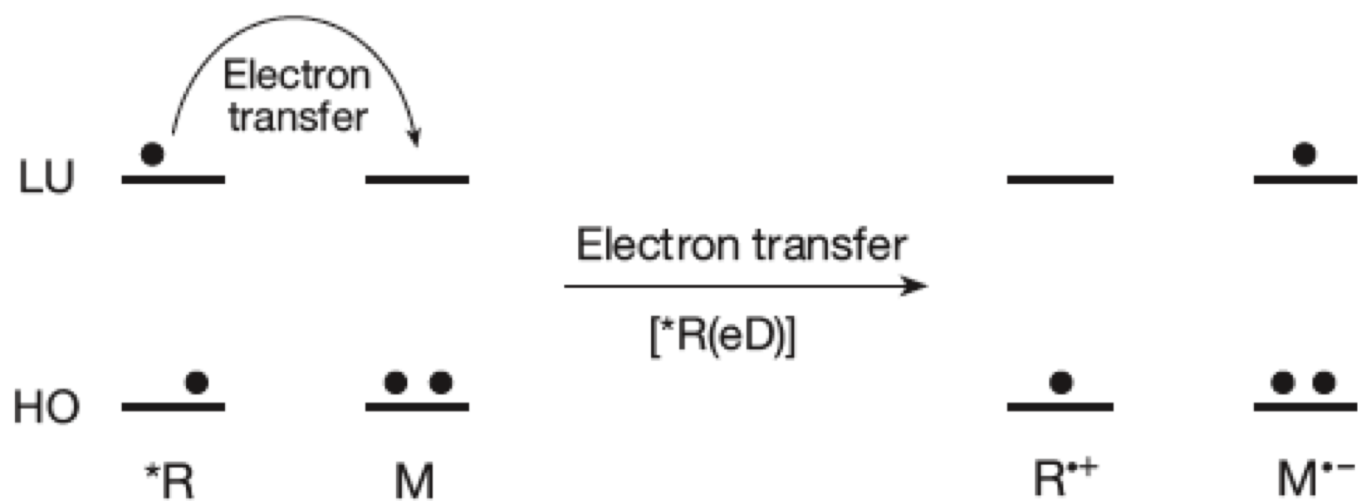
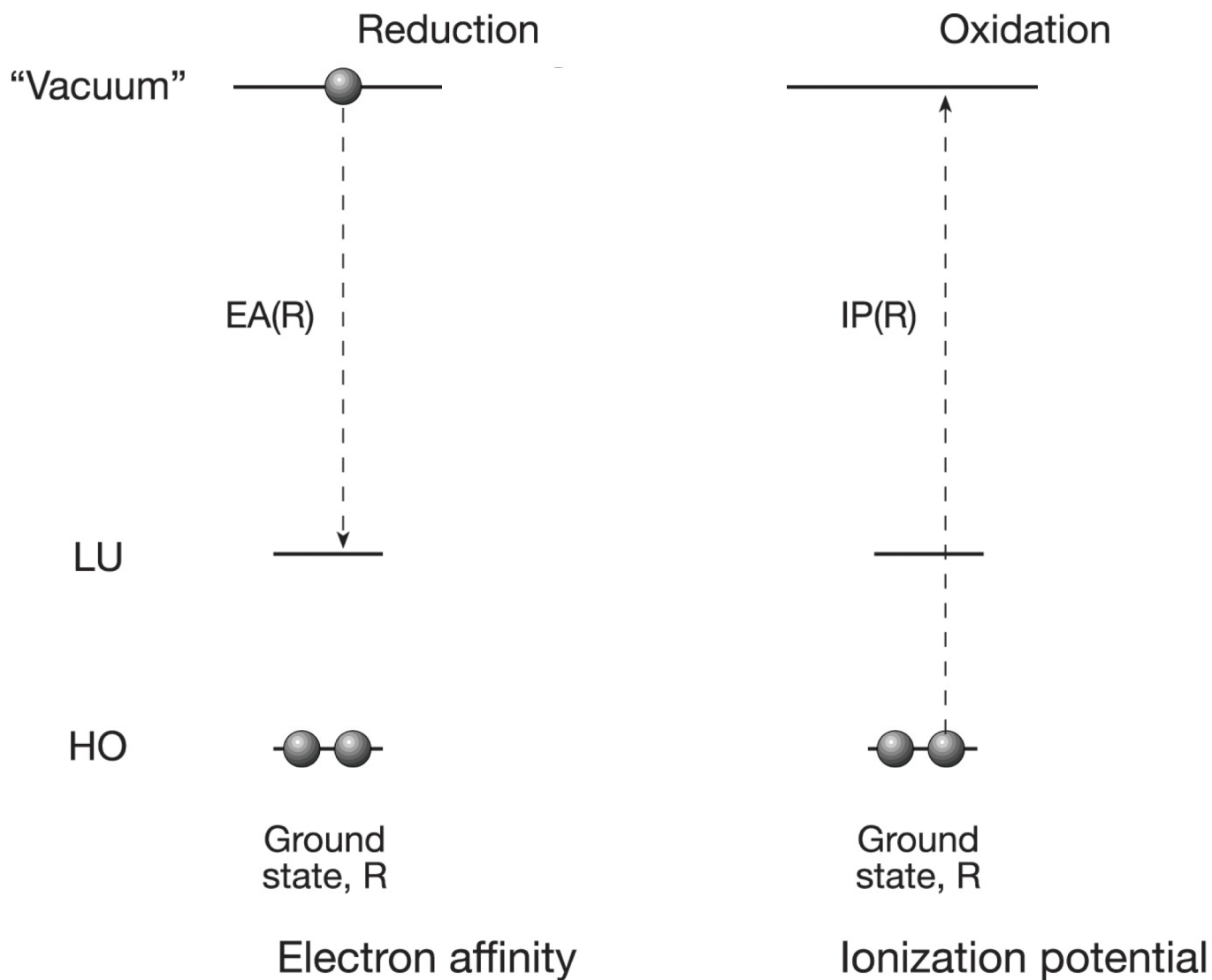$$P^{\bullet+} + sens^{\bullet-} \longrightarrow P + sens$$

Electron Transfer

Electron Addition and Removal is Easier in the Excited State than in the Ground State

Gas phase vs. solution

Gas Phase
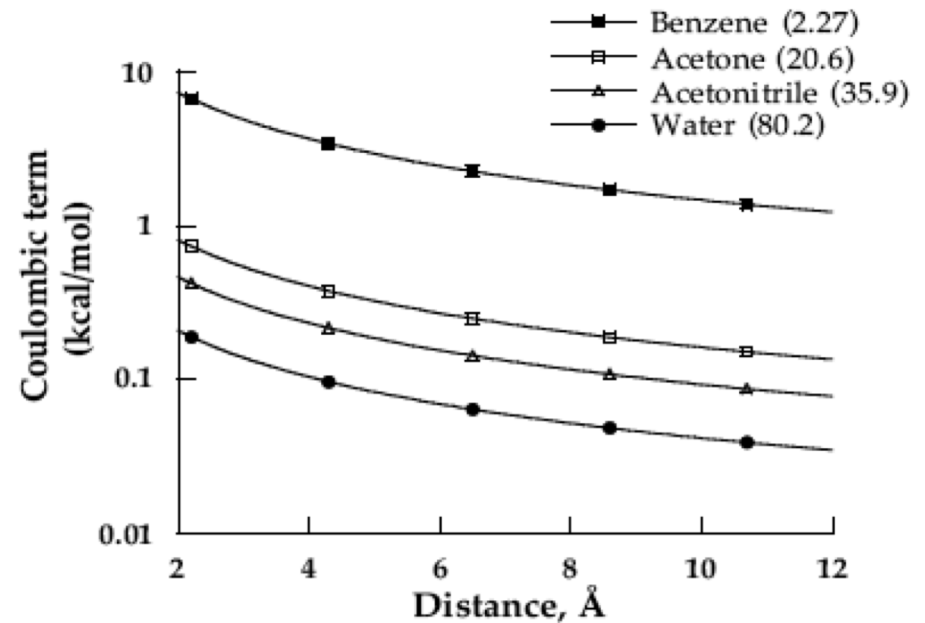
$$\Delta G = (IP)_D - (EA)_A - E_D^*$$

Solution

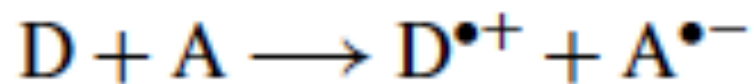$$\Delta G \approx \Im E_{D^{+\bullet}/D}^o - \Im E_{A/A^{-\bullet}}^o - E_D^*$$

Solution (with Coulombic correction)

$$\Delta G \approx \Im E_{D^{+\bullet}/D}^o - \Im E_{A/A^{-\bullet}}^o - E_D^* - N_A \frac{e^2}{4\pi\varepsilon^o \varepsilon r}$$
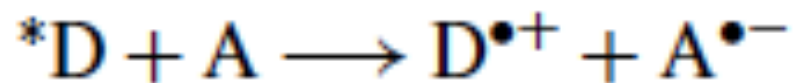
**Ground state
(gas phase)**

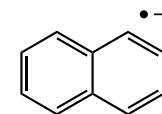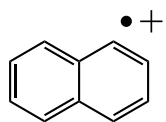$$D + A \longrightarrow D^{\bullet+} + A^{\bullet-}$$

$$\Delta G_{et} = (IP)D - (EA)A$$

**Excited state
(gas phase)**

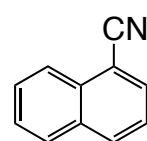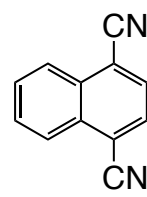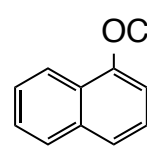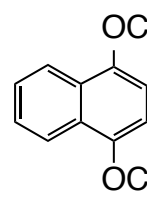$$^*D + A \longrightarrow D^{\bullet+} + A^{\bullet-}$$
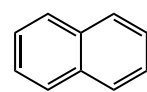
$$^*\Delta G = (IP)_D - (EA)A - E^*D$$

**Excited state
In solution**

$$\Delta G_{et} = E_{1/2}^{ox}(D) - E_{1/2}^{red}(A) - E_{exc}(A) + \Delta E_{Coulombic}$$

E_{ox} E_{red}

	E_{ox}	E_{red}
naphthalene	1.84 V	–2.5 V
1-CN naphthalene	--	–1.98 V
1,4-diCN naphthalene	--	–1.28 V
1-OCH$_3$ naphthalene	1.38 V	--
1,4-diOCH$_3$ naphthalene	1.10 V	--

$$\Delta G_{et} = E_{1/2}^{ox}(D) - E_{1/2}^{red}(A) - E_*(A) + \Delta E_{Coulombic}$$

Caution

Be careful about the sign

It is very important to note that by convention in electrochemistry, *both* $E°$ (D/D•+) and $E°$ (A/A•–) *are expressed as* <u>reductions</u> *(*D•+/D and A/A•–). Both reactions are expressed as A + e→A•– and D•+ + e→D. Because of this convention, one must pay careful attention to the signs of $E°$ (D•+/D) and $E°$ (A/A•–) when computing the overall value of ΔG.
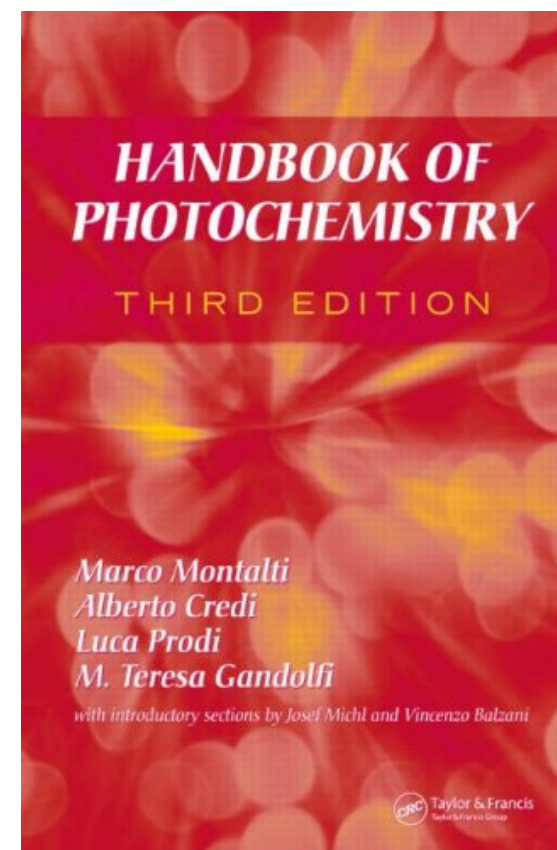
Be careful about the reference electrode

Another important point in using electrochemical data is that one must employ the standard electrode to which the values of $E°$ (D+/D) and $E°$ (A/A–) refer. Both the standard <u>hydrogen electrode </u>and the standard <u>calomel electrode and silver electrode</u> are commonly used as standards. So care must be taken to know which is being used and not to mix data from the two standards unless appropriate corrections are made.

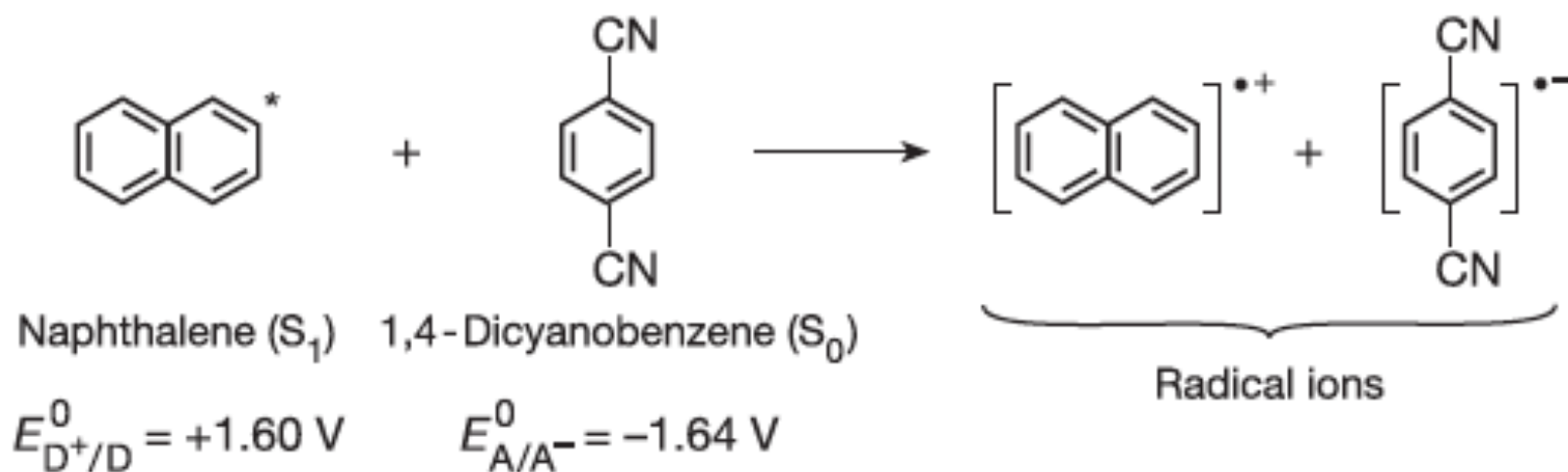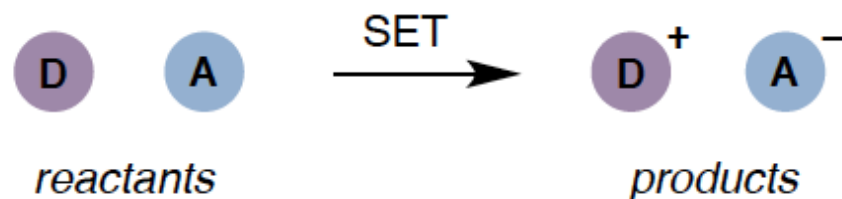## Table 7b-3 Halfwave Redox Potentials of Aromatic Hydrocarbons.

No.	Compound	$E_{1/2}(X^+/X)$ (V vs. SCE) MeCN	Ref	$E_{1/2}(X/X^-)$ (V vs. SCE) DMF	Ref
1	Acenaphthene	+1.21	[6301]	−2.67	[7001]
2	Acetylene, diphenyl-	−		−2.11	[7701]
3	Anthracene	+1.09	[6301]	−1.95	[7701]
4	Anthracene, 9,10-bis(phenylethynyl)-	+1.165	[6701]	−1.29	[6701]
5	Anthracene, 9,10-dimethyl-	+0.95	[6401]	−	
6	Anthracene, 9,10-diphenyl-	+1.22	[7701]	−1.94	[7701]
7	Anthracene, 9-methyl-	+0.96	[6301]	−1.97[a]	[6201]
8	Anthracene, 9-phenyl-	−		−1.86	[7001]
9	Azulene	+0.71	[6301]	−1.65[a]	[6201]
10	Benz[a]antracene	+1.18	[6301]	−	

Table 7b-7 Halfwave Redox Potentials of Nitriles.

No.	Compound	$E_{1/2}(A/A^-)$ (V vs. Ag electrode) DMF[a]	$E_{1/2}(A/A^-)$ (V vs. SCE) MeCN
1	Anthracene, 9-cyano-	−	−1.58[b]
2	Anthracene, 9,10-dicyano-	−	−0.98[b]
3	Benzene, 1-cyano-3,5-dinitro-	−0.96	−
4	Benzene, 1-cyano-4-nitro-	−1.25	−
5	Benzene, 1,2-dicyano-	−2.12	−

SET

reactants → products

Naphthalene (S_1)   1,4-Dicyanobenzene (S_0)

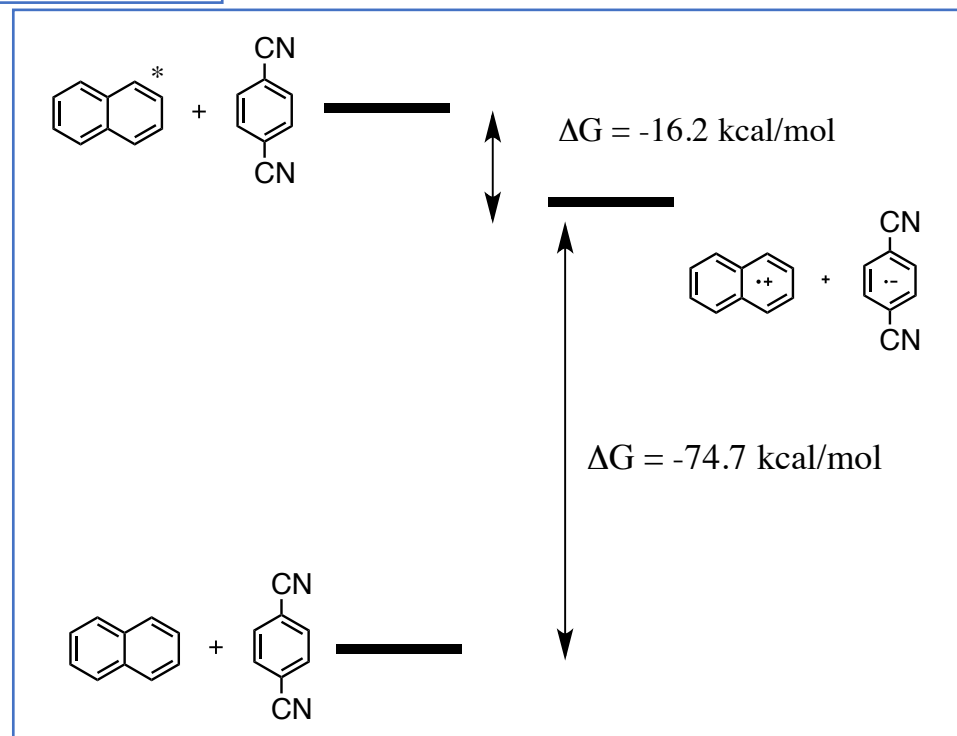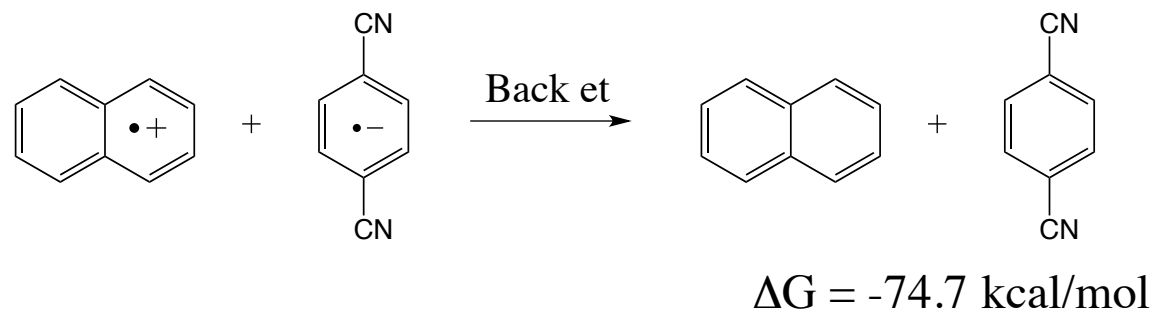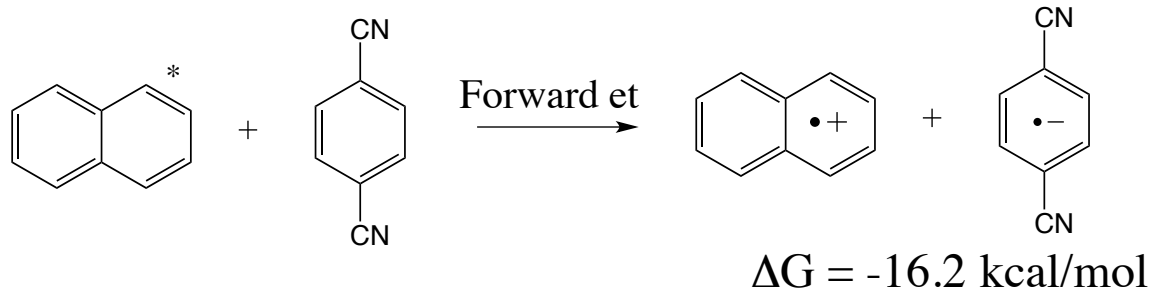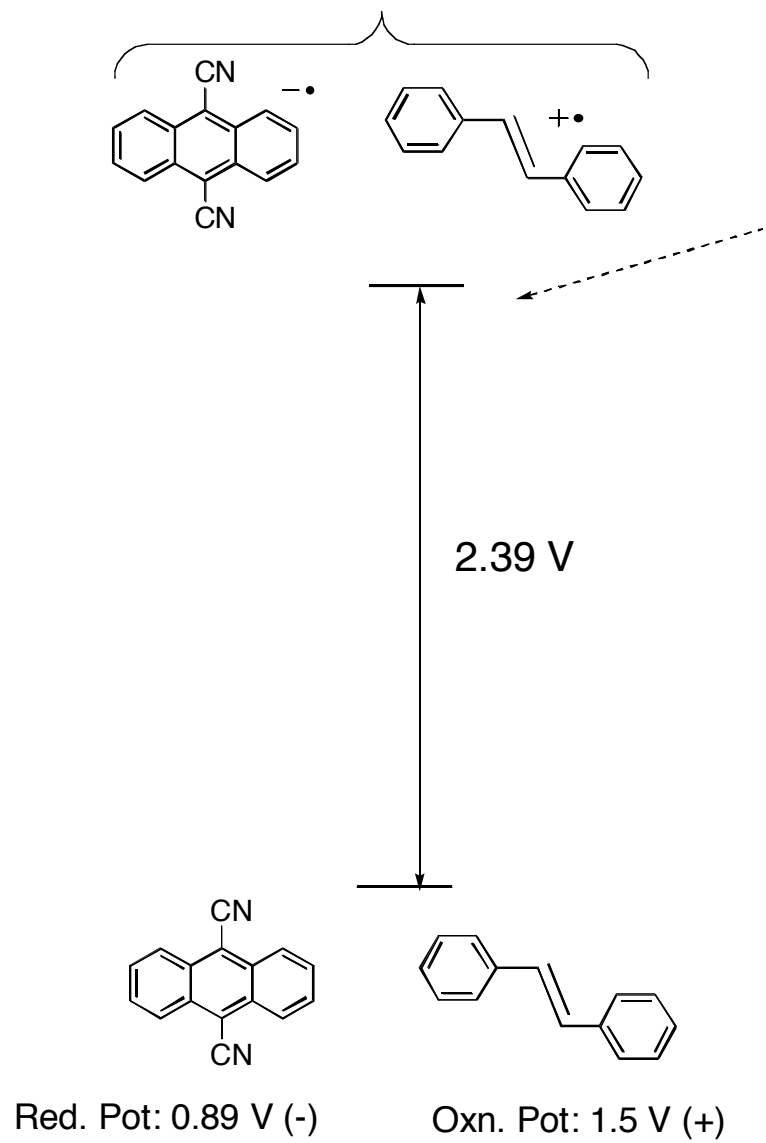Radical ions

$E^0_{D^+/D} = +1.60$ V $E^0_{A/A^-} = -1.64$ V

$$E(S_1) = 3.94 \text{ eV} = 90.9 \text{ kcal mol}^{-1}$$

$$\Delta G° = \mathcal{F}E^0_{D^+/D} - \mathcal{F}E^0_{A/A^-} - E^*_D - 0.2$$

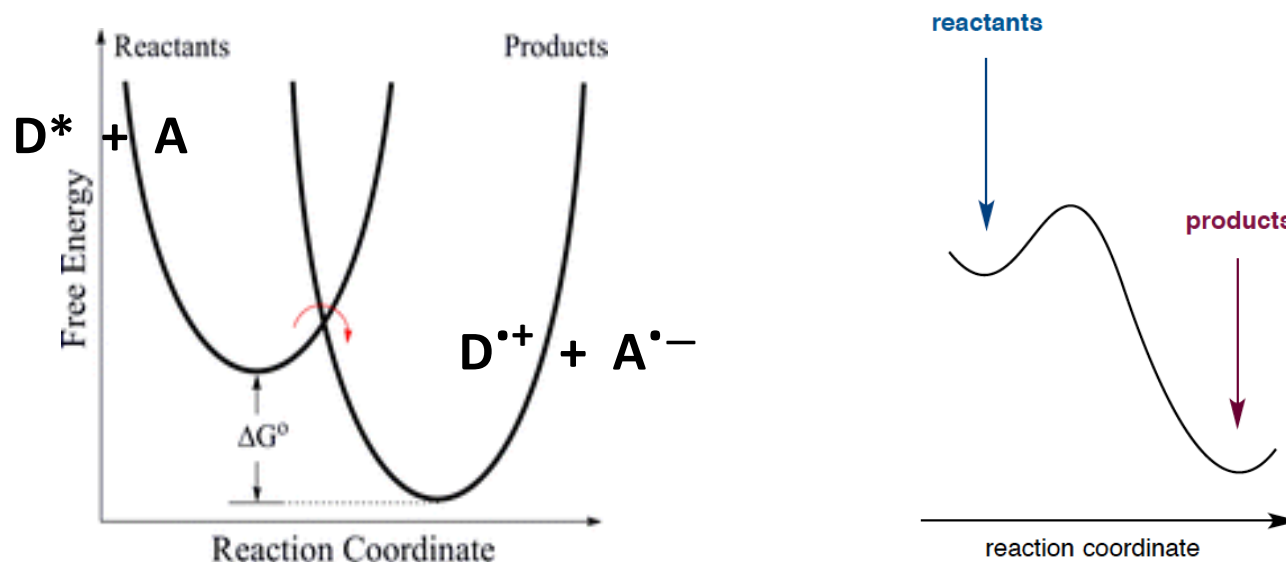$$\Delta G° = 36.9 - (-37.8) - 90.9 - 0.2 = -16.4 \text{ kcal mol}^{-1}$$

$$k \text{ (electron transfer)} = 1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

Forward et

$\Delta G = -16.2$ kcal/mol

Back et

$\Delta G = -74.7$ kcal/mol

$\Delta G = -16.2$ kcal/mol

$\Delta G = -74.7$ kcal/mol

CN

–•

+•

2.39 V

CN

CN

Red. Pot: 0.89 V (-)   Oxn. Pot: 1.5 V (+)

Free energy of activation expressed in terms of the free energy of reaction (ΔG) and free energy of activation (ΔG#)
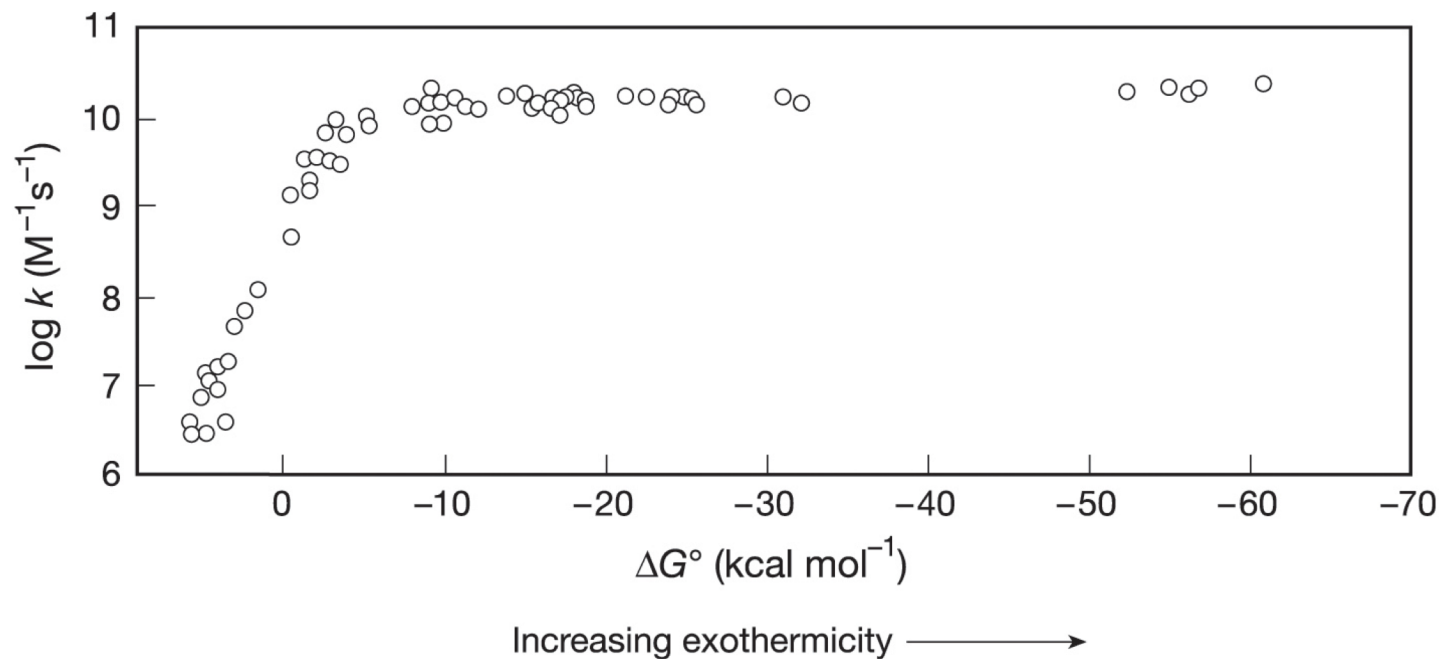

$$k_{et} = k_0 \exp\left(-\frac{\Delta G^{\ddagger}_{et}}{RT}\right)$$

$$\Delta G_{et} = E^{ox}_{1/2}(D) - E^{red}_{1/2}(A) - E_*(A) + \Delta E_{Coulombic}$$

Rehm-Weller Equation

Dependence of the electron transfer rate on the driving force ΔG^0 and the free energy of activation $\Delta G^{\ddagger}$

D. Rehm and A. Weller, *Isr. J. Chem., 8*, 259, **1970**

A. Weller

Rehm-Weller Plot

The value of k_{et} reaches a plateau value of $\sim 2 \times 10^{10}$ M^{-1}s^{-1} after an exothermicity of $\sim$ -10 kcal mol^{-1} and the value of k_{et} remains the diffusion controlled value to the highest negative values of achievable.
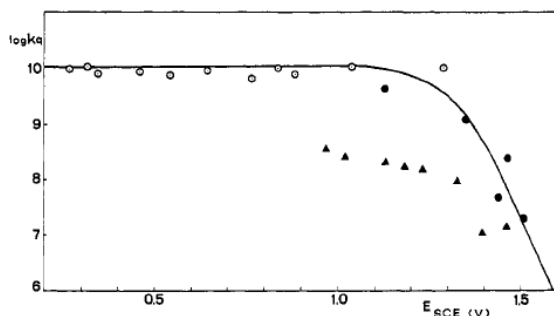
More Rehm-Weller Plots

Figure 2. Plot of the logarithm of the rate constant vs. $E_{1/2}(Q/Q^+)$ for the quenching of Cr(bpy)$_3$$^{3+}$ by aromatic amines (⊙), methoxybenzenes (●), and aliphatic amines (▲).
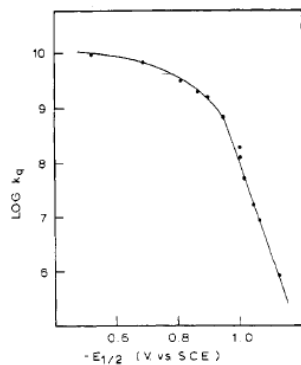
V. Balzani, et. al., *JACS, 100*, 7219, **1978**

Figure 1. Plot of log k_q^{obsd} vs. quencher reduction potential, $E_{1/2}[Q/Q^-]$.

C. R. Brock, T. J. Myers and
D. G. Whitten, et. al.,
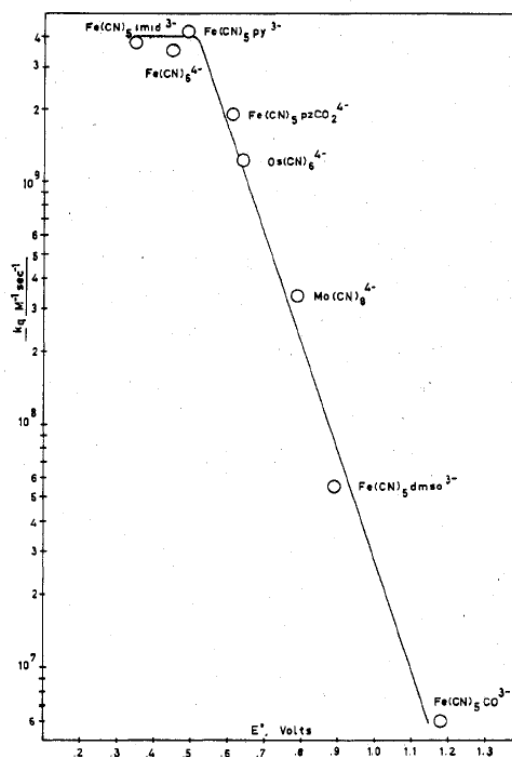*JACS, 97*, 2909, **1975**

Figure 4. Dependence of quenching rate constant on quencher redox potential for several metallocyanide complexes.
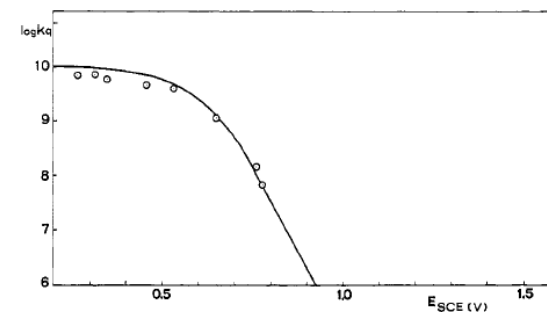
H. Toma and C. Creutz ,
*Inorganic Chemistry,
16*, 545, **1977**

Figure 3. Plot of the logarithm of the rate constant vs. $E_{1/2}(Q/Q^+)$ for the quenching of Ru(bpy)$_3$$^{2+}$ by aromatic amines.
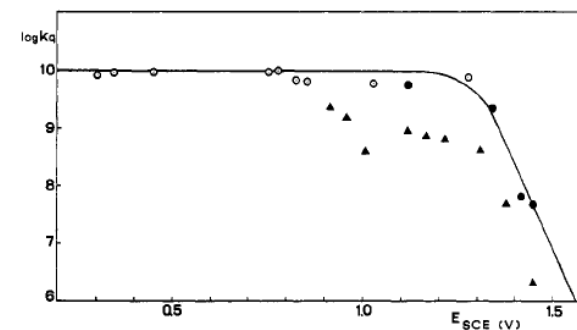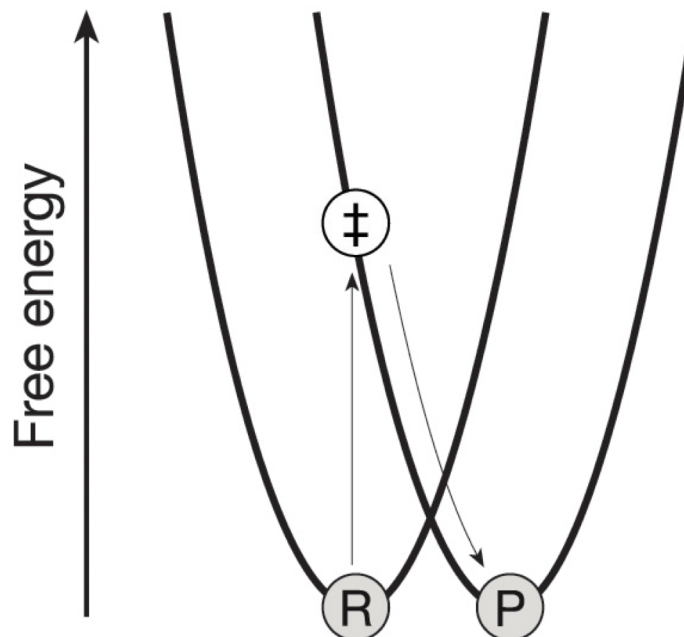

Figure 4. Plot of the logarithm of the rate constant vs. $E_{1/2}(Q/Q^+)$ for the quenching of Ir(Me$_2$phen)$_2$Cl$_2$$^+$ by aromatic amines (⊙), methoxybenzenes (●), and aliphatic amines (▲).
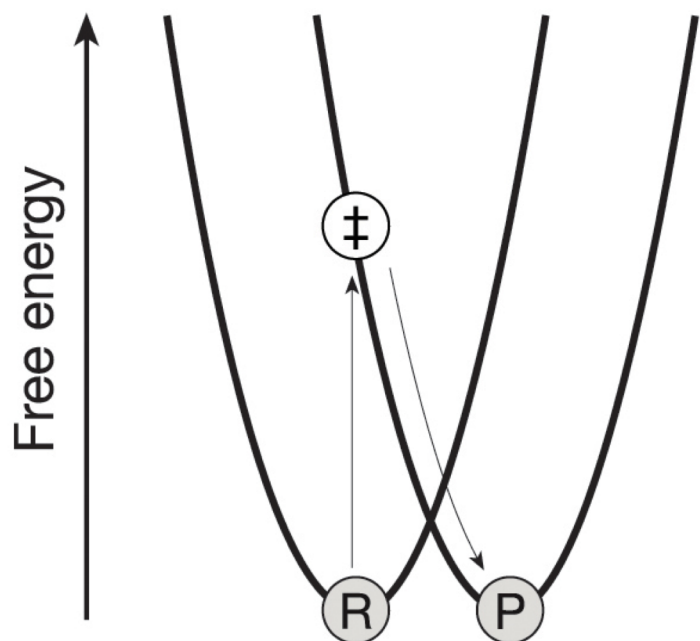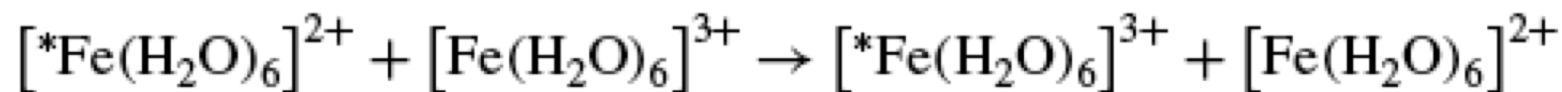
Libby Model

Willard F. Libby

The Nobel Prize in Chemistry 1960 was awarded to Willard F. Libby "for his method to use carbon-14 for age determination in archaeology, geology, geophysics, and other branches of science".
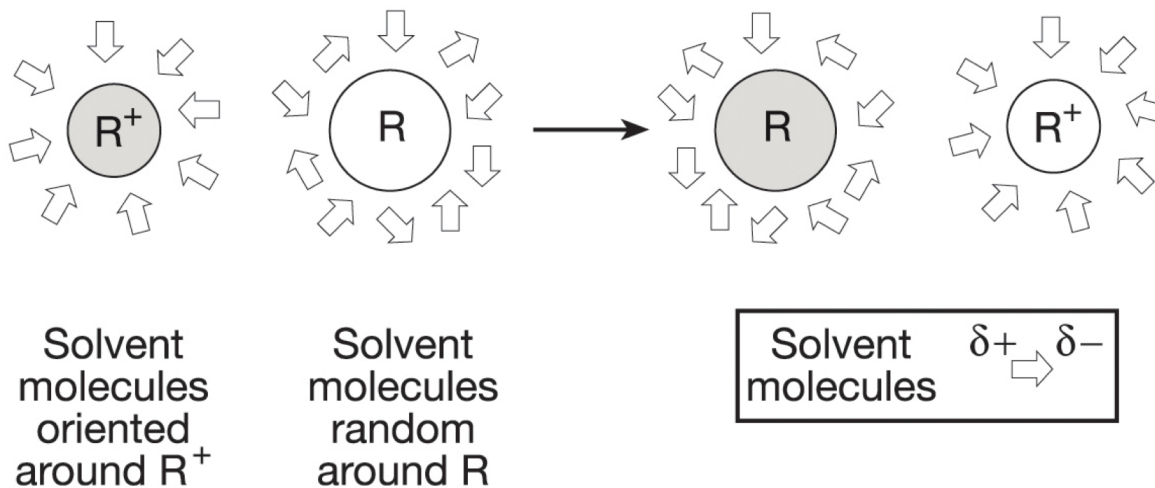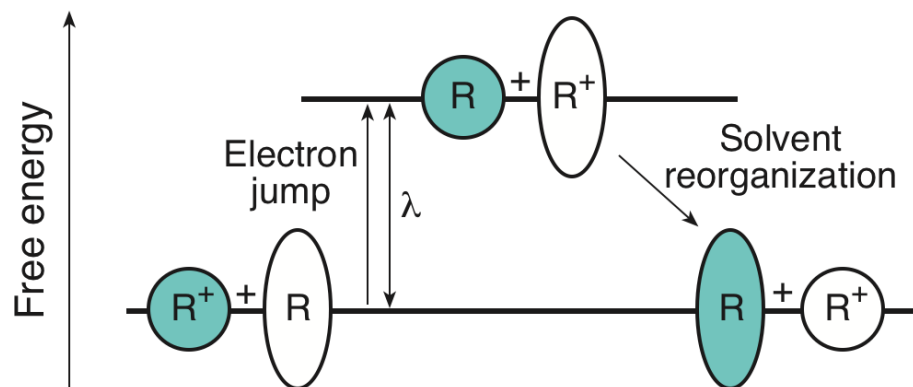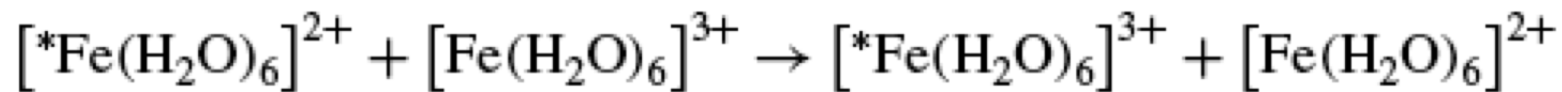
Libby Model

$$R^{\bullet+}(\text{solvated}) + R(\text{solvated}) \rightarrow R(\text{solvated}) + R^{\bullet+}(\text{solvated})$$

$$\left[{}^{*}Fe(H_2O)_6\right]^{2+} + \left[Fe(H_2O)_6\right]^{3+} \rightarrow \left[{}^{*}Fe(H_2O)_6\right]^{3+} + \left[Fe(H_2O)_6\right]^{2+}$$

The electron jump from R* to $R^{\bullet+}$ is analogous to the electron jump from a HO to a LU that leads to formation of an electronically excited state.

The electron jump is expected to occur "vertically" and to follow the Franck-Condon principle; the geometry of the products formed by an electron transfer would be the same as the geometry of the reactants.
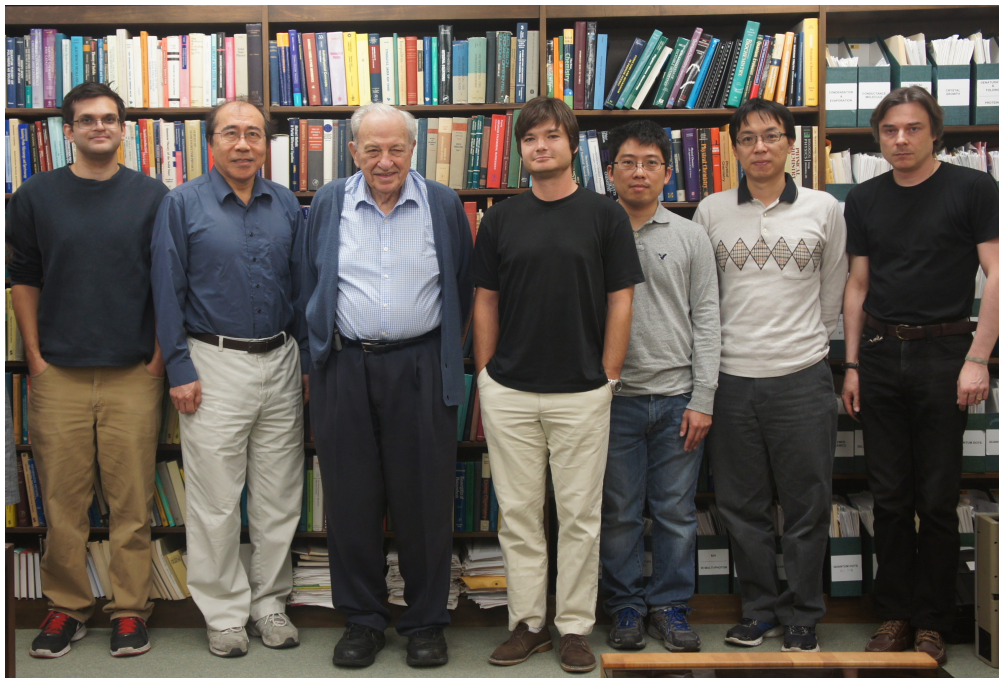
Two types of reorganization occur after the et: (1) an electronic and vibrational reorganization, termed *internal molecular reorganization*; and (2) a solvent reorganization associated with the solvent reorientation to accommodate the new electronic structures termed *external solvent reorganization*.

Libby Model

$$R^{\bullet+}(\text{solvated}) + R(\text{solvated}) \rightarrow R(\text{solvated}) + R^{\bullet+}(\text{solvated})$$

$$\left[{}^*\text{Fe}(\text{H}_2\text{O})_6\right]^{2+} + \left[\text{Fe}(\text{H}_2\text{O})_6\right]^{3+} \rightarrow \left[{}^*\text{Fe}(\text{H}_2\text{O})_6\right]^{3+} + \left[\text{Fe}(\text{H}_2\text{O})_6\right]^{2+}$$

Marcus Theory

On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I*

R. A. MARCUS

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York

(Received July 28, 1955)

A mechanism for electron transfer reactions is described, in which there is very little spatial overlap of the electronic orbitals of the two reacting molecules in the activated complex. Assuming such a mechanism, a quantitative theory of the rates of oxidation-reduction reactions involving electron transfer in solution is presented. The assumption of "slight-overlap" is shown to lead to a reaction path which involves an intermediate state X^* in which the electrical polarization of the solvent does not have the usual value appropriate for the given ionic charges (i.e., it does not have an equilibrium value). Using an equation developed elsewhere for the electrostatic free energy of nonequilibrium states, the free energy of all possible intermediate states is calculated. The characteristics of the most probable state are then determined with the aid of the calculus of variations by minimizing its free energy subject to certain restraints. A simple expression for the electrostatic contribution to the free energy of formation of the intermediate state from the reactants, ΔF^*, is thereby obtained in terms of known quantities, such as ionic radii, charges, and the standard free energy of reaction.

This intermediate state X^* can either disappear to reform the reactants, or by an electronic jump mechanism to form a state X in which the ions are characteristic of the products. When the latter process is more probable than the former, the over-all reaction rate is shown to be simply the rate of formation of the intermediate state, namely the collision number in solution multiplied by $\exp(-\Delta F^*/kT)$. Evidence in favor of this is cited. In a detailed quantitative comparison, given elsewhere, with the kinetic data, no arbitrary parameters are needed to obtain reasonable agreement of calculated and experimental results.

R. A. Marcus, *J. Chem. Phys.*, *24*, 966, **1956**.

R. A. Marcus and N. Sutin, *Biochemica et Biophysica Acta*, *811*, 265, **1985**.

R. A. Marcus, *Electron transfer Reactions in Chemistry: Theory and Experiment,* (Nobel Lecture) *Angew. Chem. Int. Ed.*, *32*, 1111, **1993**.
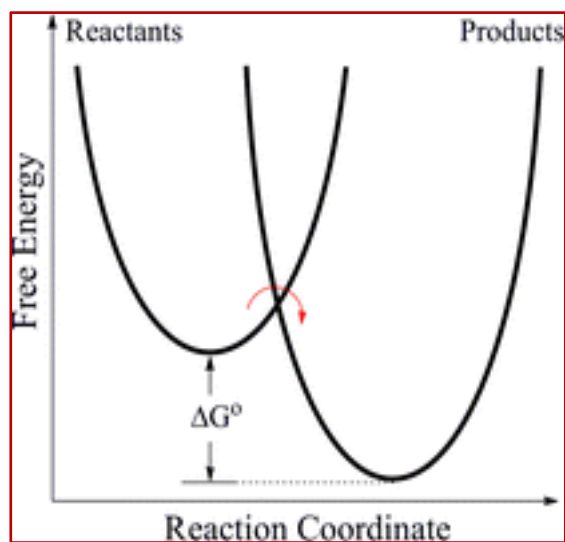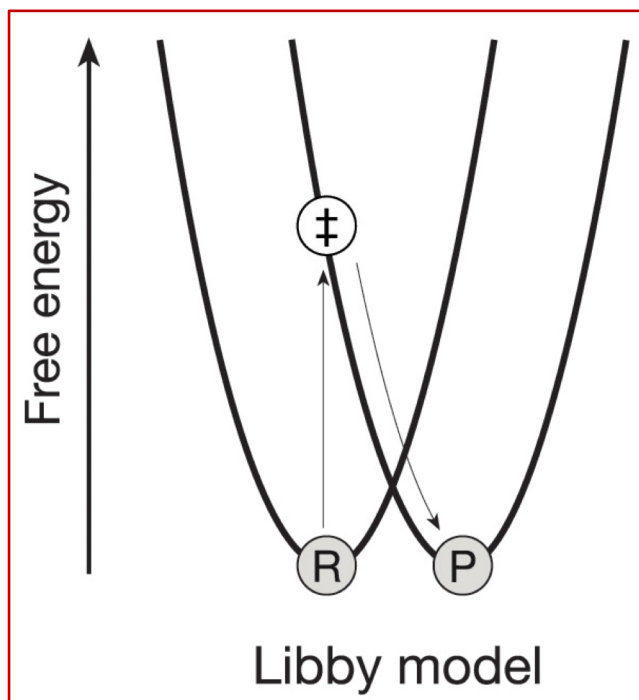
R. A. Marcus

Rates are expected:

✧ to be slow for weakly exothermic reactions,

✧ to increase to a maximum for moderately exothermic reactions, and then

✧ **to decrease with increasing exothermicity for highly exothermic et reactions.**

Evolution of Marcus model

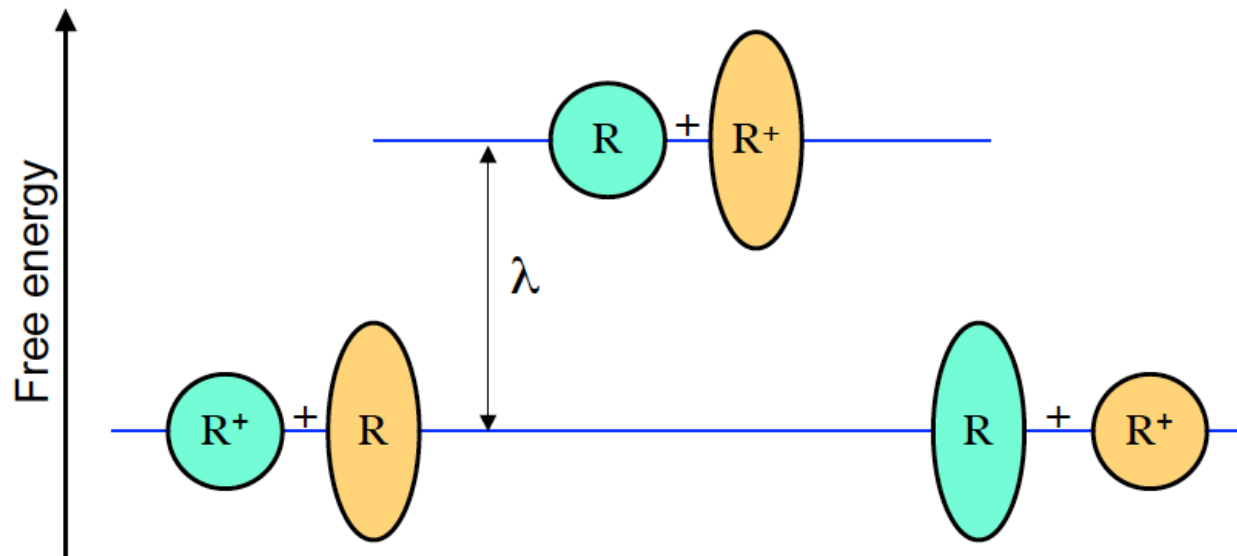R. A. Marcus, *J. Chem. Phys.*, *24*, 966, **1956**.

Weller Model

Libby model

Marcus model

$$k_{et} = A \, exp^{-(\Delta G\ddagger/RT)}$$
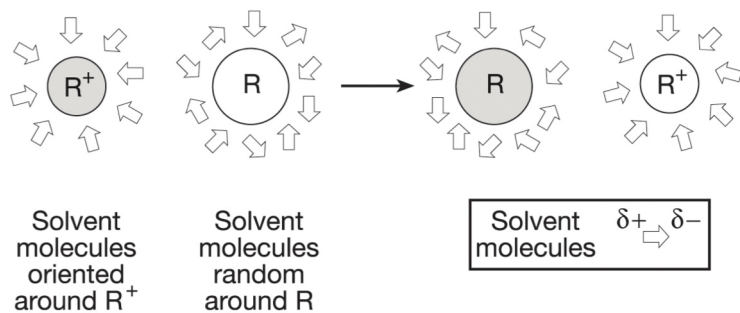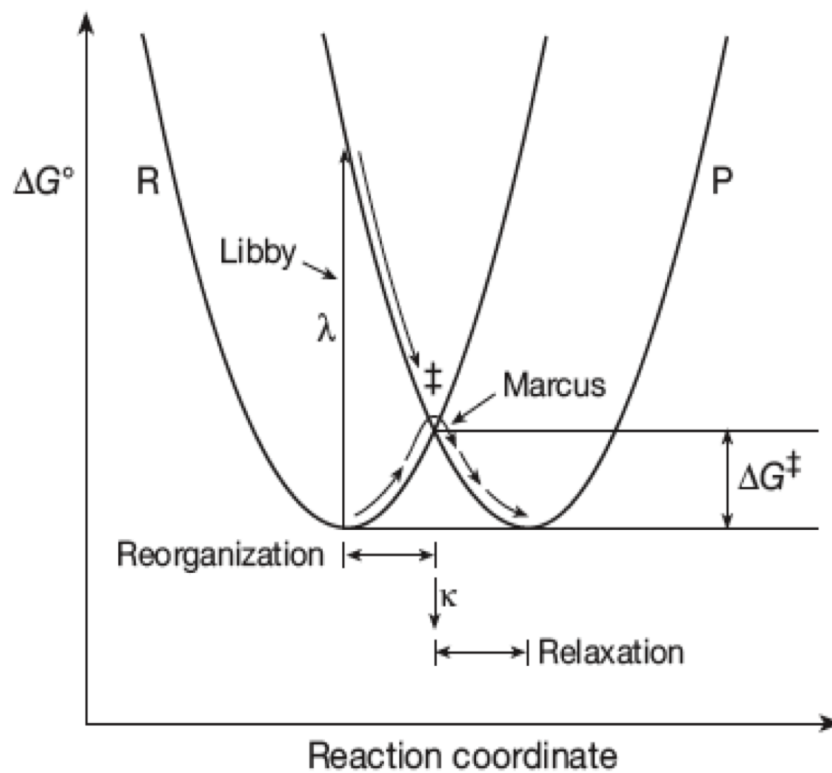
Libby Model

Electron transfer is a two step process:

    (a) Electron transfer first with no change of nuclear positions (Franck-Condon principle)

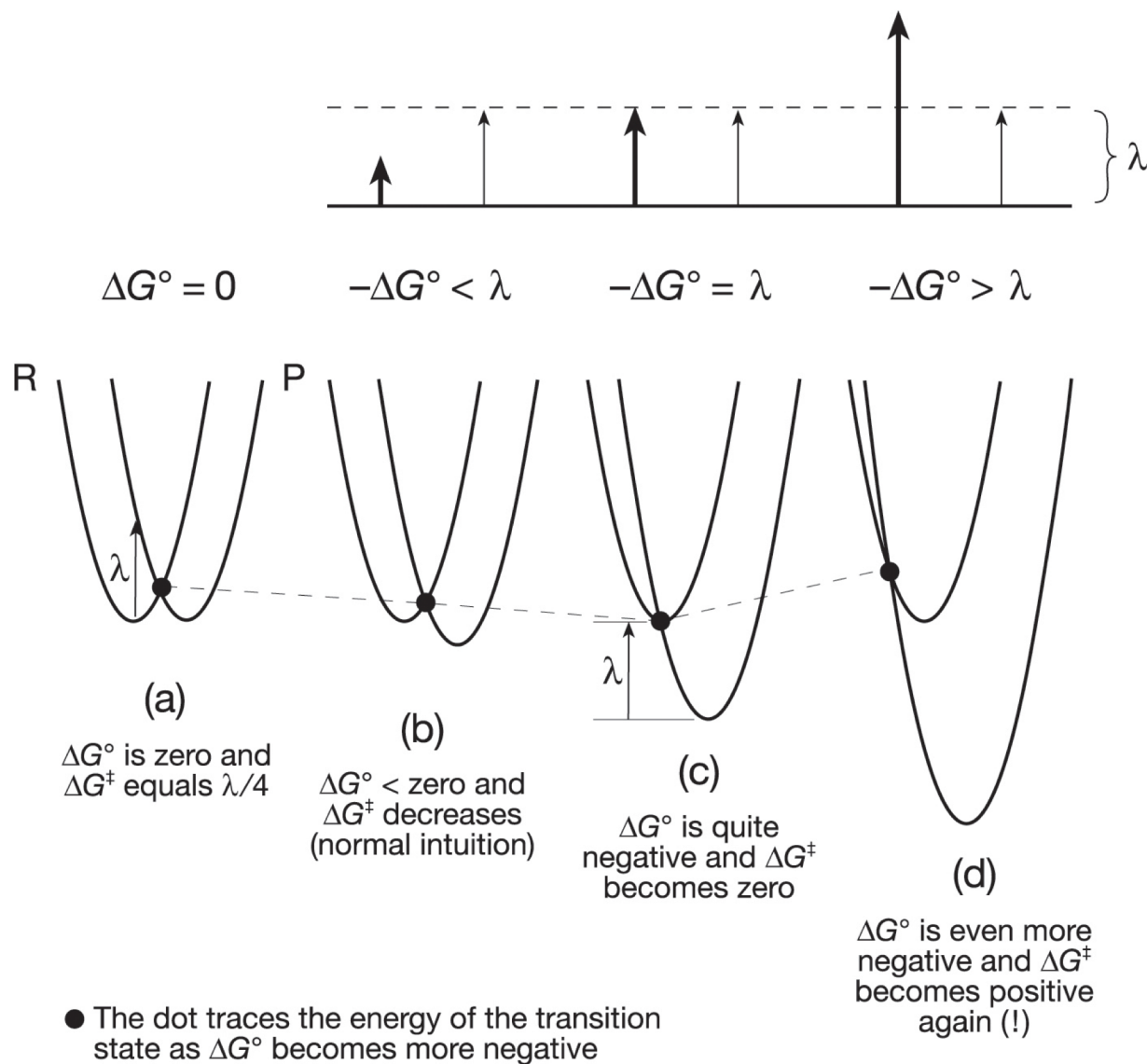   **(b) Solvent reorganization**

Marcus Model

The above two step model violates thermodynamic principle of conservation of energy.
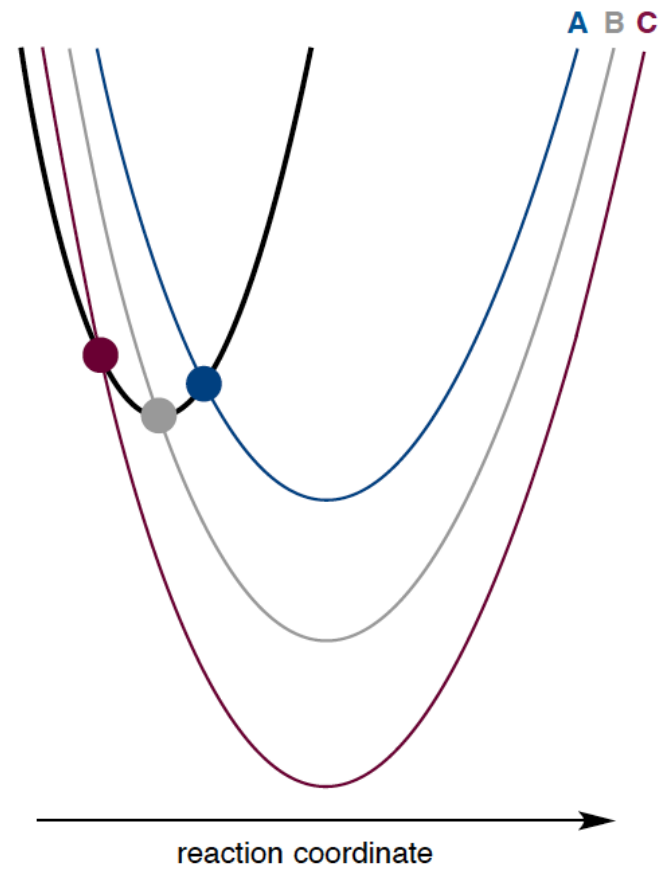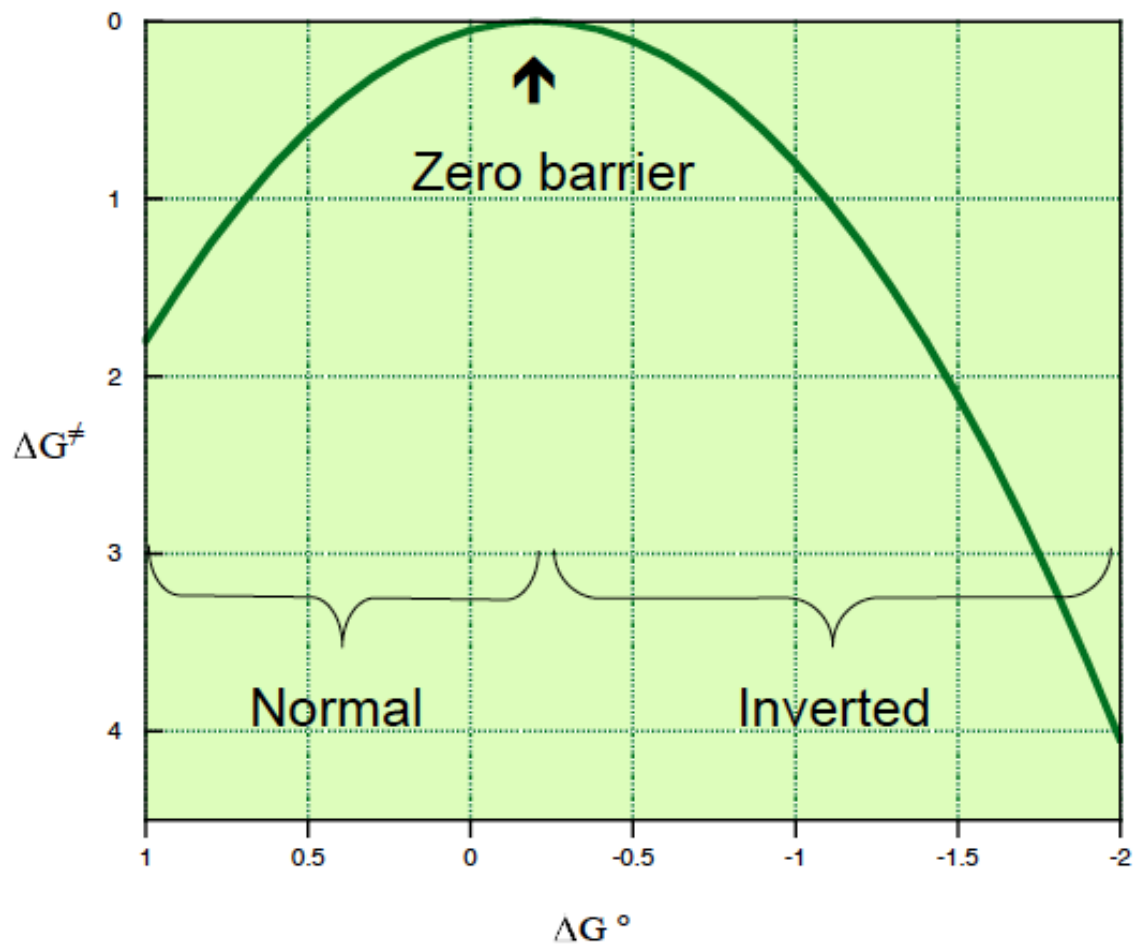
The Marcus model

The re-emergence of the activation barrier ($\Delta G^{\ddagger}$) at large negative ΔG^0 values

$\Delta G° = 0$ $-\Delta G° < \lambda$ $-\Delta G° = \lambda$ $-\Delta G° > \lambda$

(a)
$\Delta G°$ is zero and
$\Delta G^{\ddagger}$ equals $\lambda/4$

(b)
$\Delta G° <$ zero and
$\Delta G^{\ddagger}$ decreases
(normal intuition)

(c)
$\Delta G°$ is quite
negative and $\Delta G^{\ddagger}$
becomes zero

(d)
$\Delta G°$ is even more
negative and $\Delta G^{\ddagger}$
becomes positive
again (!)

● The dot traces the energy of the transition
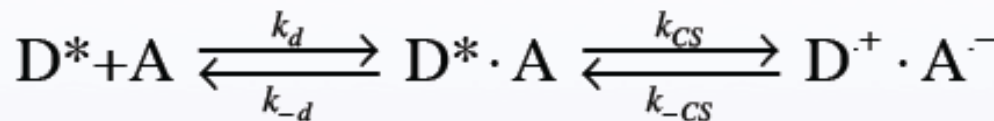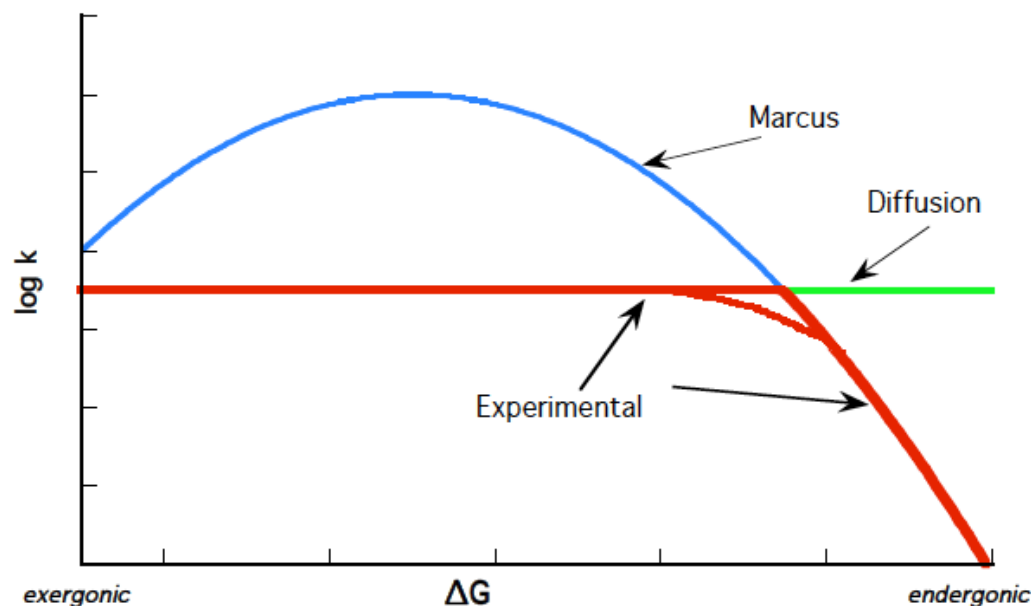state as $\Delta G°$ becomes more negative

Marcus Prediction

Marcus prediction vs Weller's experiments

The experimental rate constant is limited by the diffusion rate constant in the solvent, it effectively hides the Marcus inverted region. On the right section of the plot the reaction is endothermic and the prediction of the Marcus equation is followed. The Rehm-Weller equation does not make allowance for an inverted region.

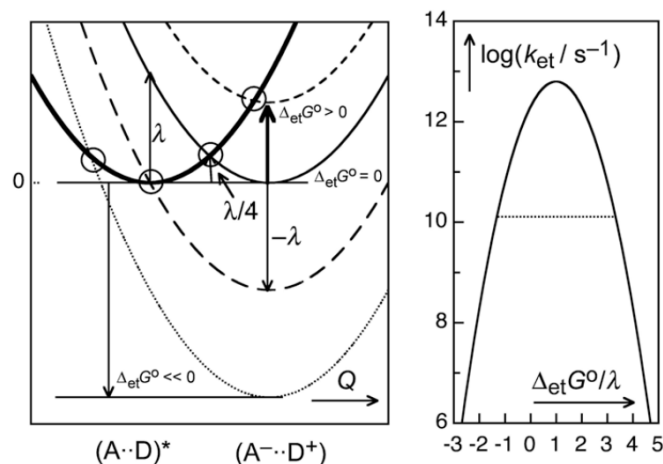# Marcus prediction vs Weller's experiments

Electron Transfer Involves Two Steps

$$D*+A \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} D* \cdot A \underset{k_{-CS}}{\overset{k_{CS}}{\rightleftharpoons}} D^+ \cdot A^-$$

The experimental rate constant is limited by the diffusion rate constant in the solvent, it effectively hides the Marcus inverted region. On the right section of the plot the reaction is endothermic and the prediction of the Marcus equation is followed. The Rehm-Weller equation does not make allowance for an inverted region.

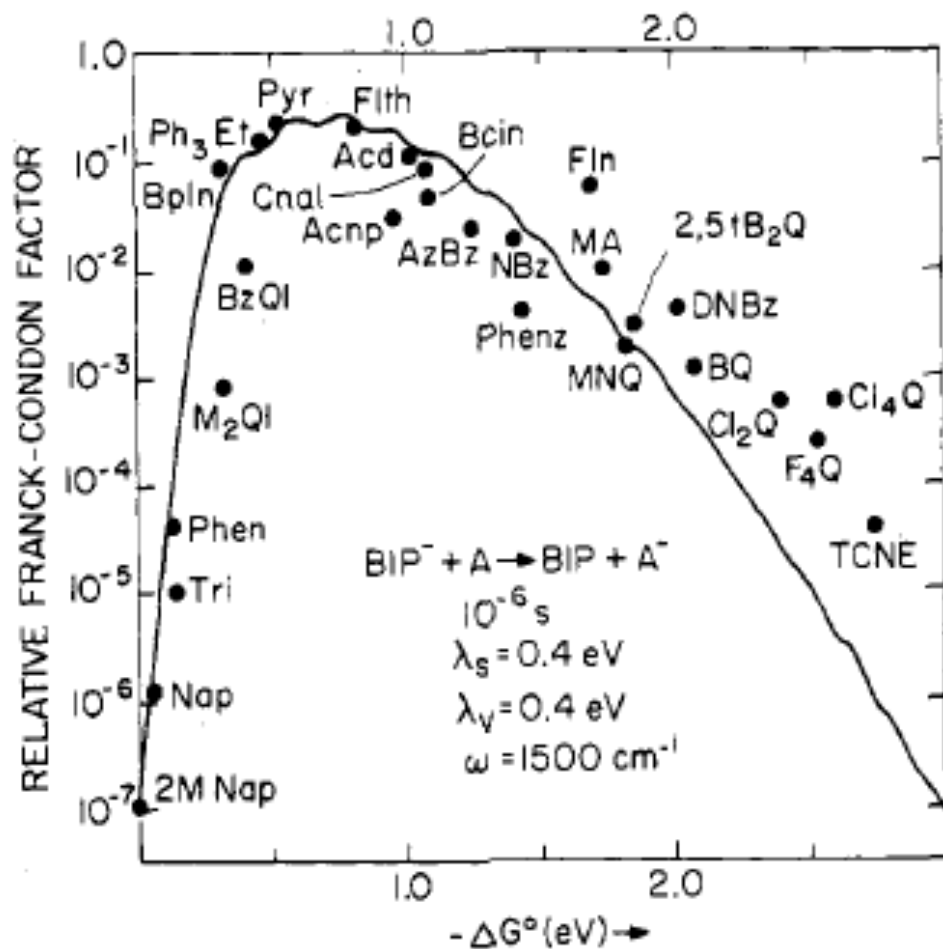# Experimental conditions to observe the Marcus "inverted region"?

For most donor-acceptor (DA) systems the inverted region is obscured by the diffusion limit.
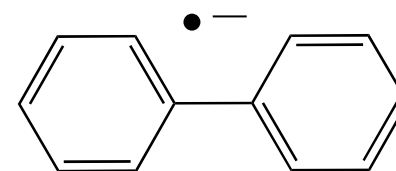
This can be circumvented by:

- ❖ freezing the donor-acceptor distribution (glassy medium)
- ❖ covalently linking the donor and the acceptor
- ❖ lowering the donor-acceptor interaction (electronic coupling V) so that the maximum rate for $-\Delta G^0 = \lambda$ is **lower** than the diffusion limit.

Effect of Free Energy on Rates of Electron Transfer Between Molecules in Glass at 77 ° K

Figure 7. Relative rates of ET reactions of the biphenyl anion as a function of exothermicity at 10^{-6} s expressed as relative Franck–Condon factors (see eq 4, 10, 11, and 12). The line was calculated by using eq 4.

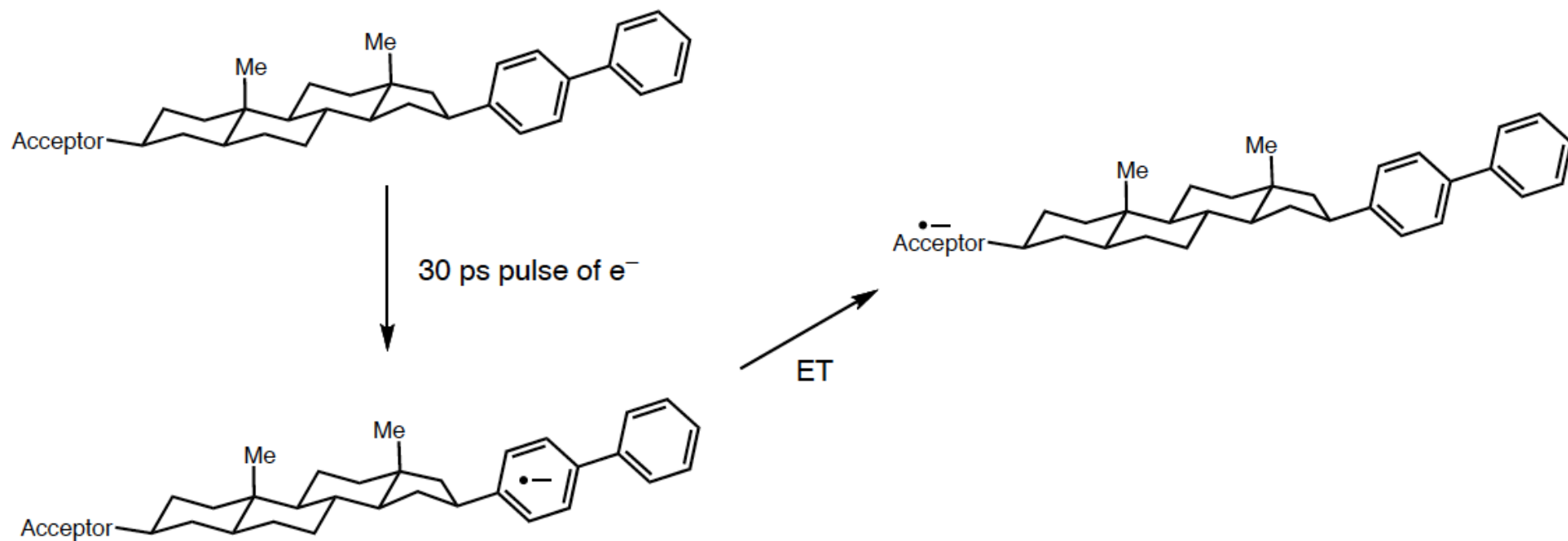J. R. Miller, J. V. Beitz, and R. K. Huddleston, *J. Am. Chem. Soc.*, *106*, 5057, **1984**.

■ Pioneering 1984 Study by Miller and Closs Definitively Proved the Existence of the Inverse Region
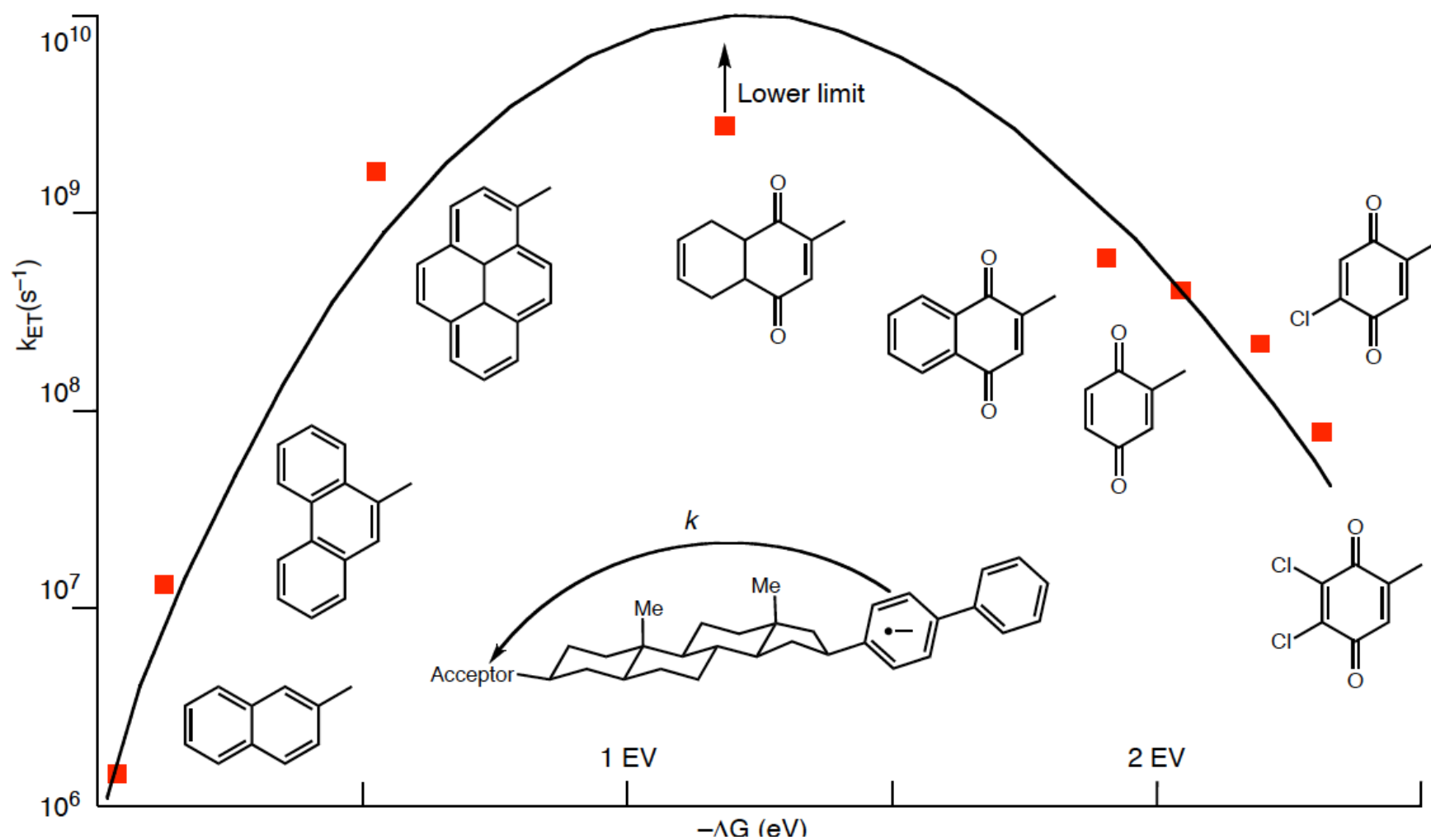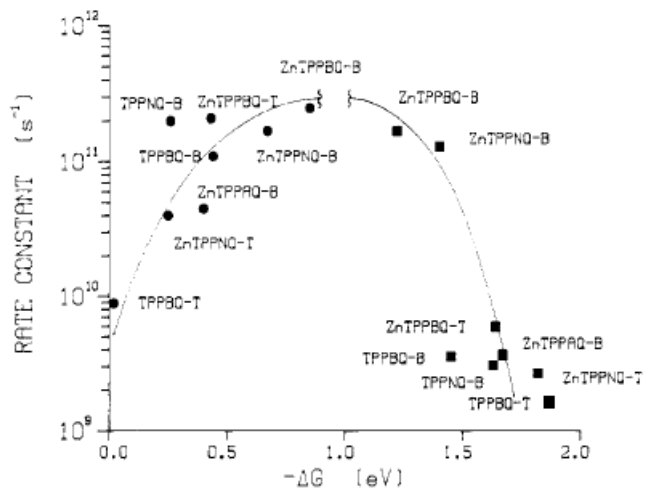
G. Closs

J. R. Miller
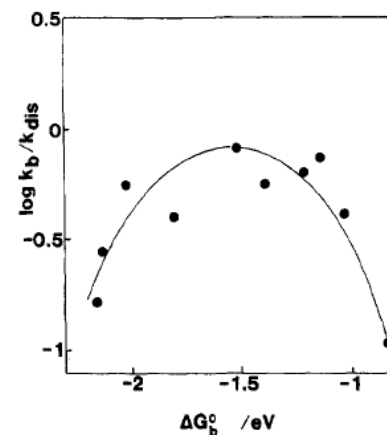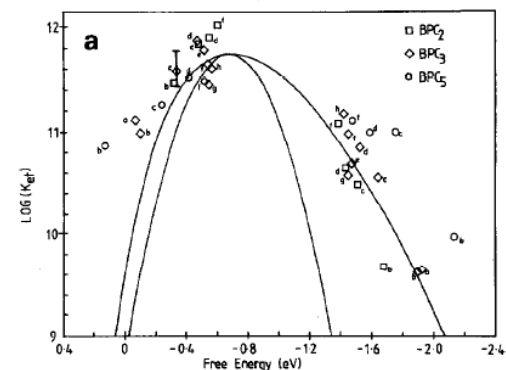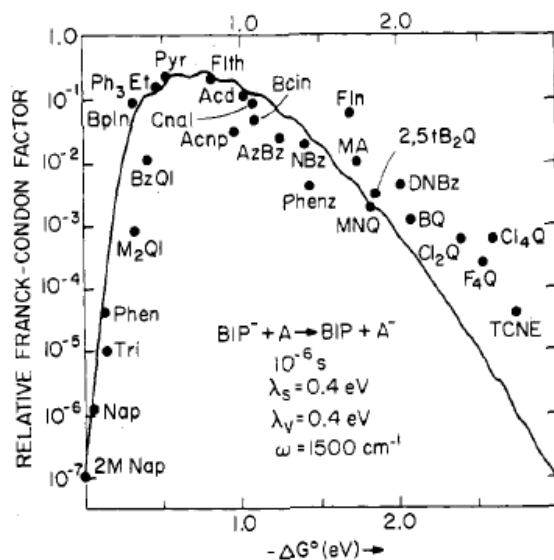
30 ps pulse of e⁻

ET

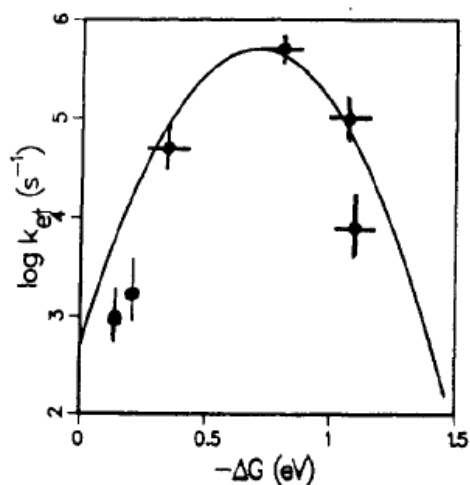G. Closs and J. R. Miller, *Science*, *240*, 440-447 (**1988**)

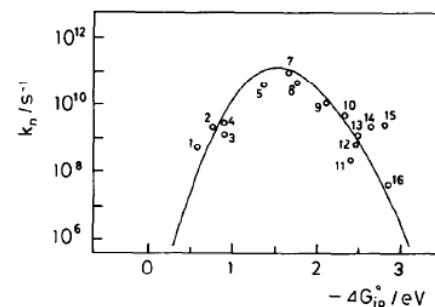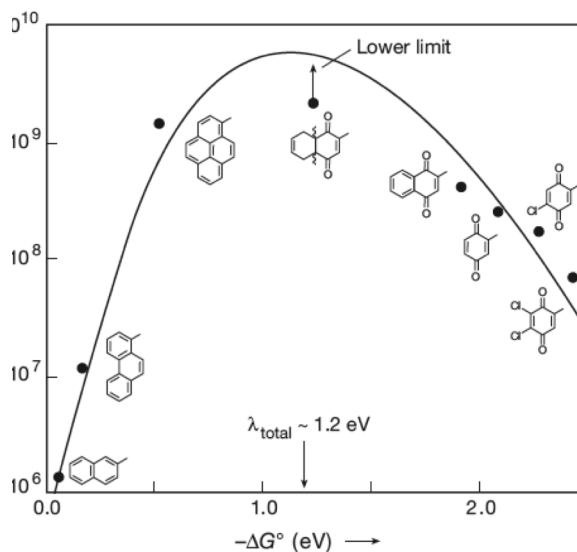J. R. Miller, L. T. Calcaterra and G. L. Closs, *J. Am. Chem. Soc.*, *106*, 3047-3049 (**1984**)

Figure 2. Plot of rate constant vs. exothermicity for the reaction $^1*P-Q \rightarrow P^+ - Q^-$ and for $P^+ - Q^- \rightarrow P - Q$, where P = porphyrin and Q = quinone. The B and T after the name of the compounds indicate data obtained in butyronitrile or in toluene, respectively. The maximum uncertainty in any given rate constant is ±20%.

$BIP^- + A \rightarrow BIP + A^-$
10^{-6} s
$\lambda_s = 0.4$ eV
$\lambda_V = 0.4$ eV
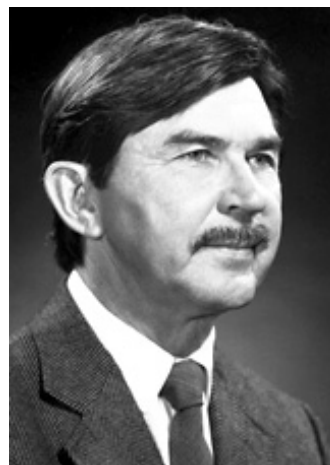$\omega = 1500$ cm^{-1}

Figure 8. Plot of intracomplex electron-transfer rate between cyt c and cyt b_5 as a function of free energy. Solid line is fit to Marcus' theory, $\lambda = 0.8v$.

Lower limit

$\lambda_{total} \sim 1.2$ eV

e 8. $\Delta G°$ dependence of k_b/k_{dis} for backward ET between Ru-$_3^+$ and the cation radicals of the aromatic donors. The line is drawn isy viewing.

Fig. 10. The dependence of the CR rate constant k_n of geminate ion pairs produced by fluorescence quenching reaction on the free energy gap $-\Delta G_{ip}^0$ in acetonitrile solution.
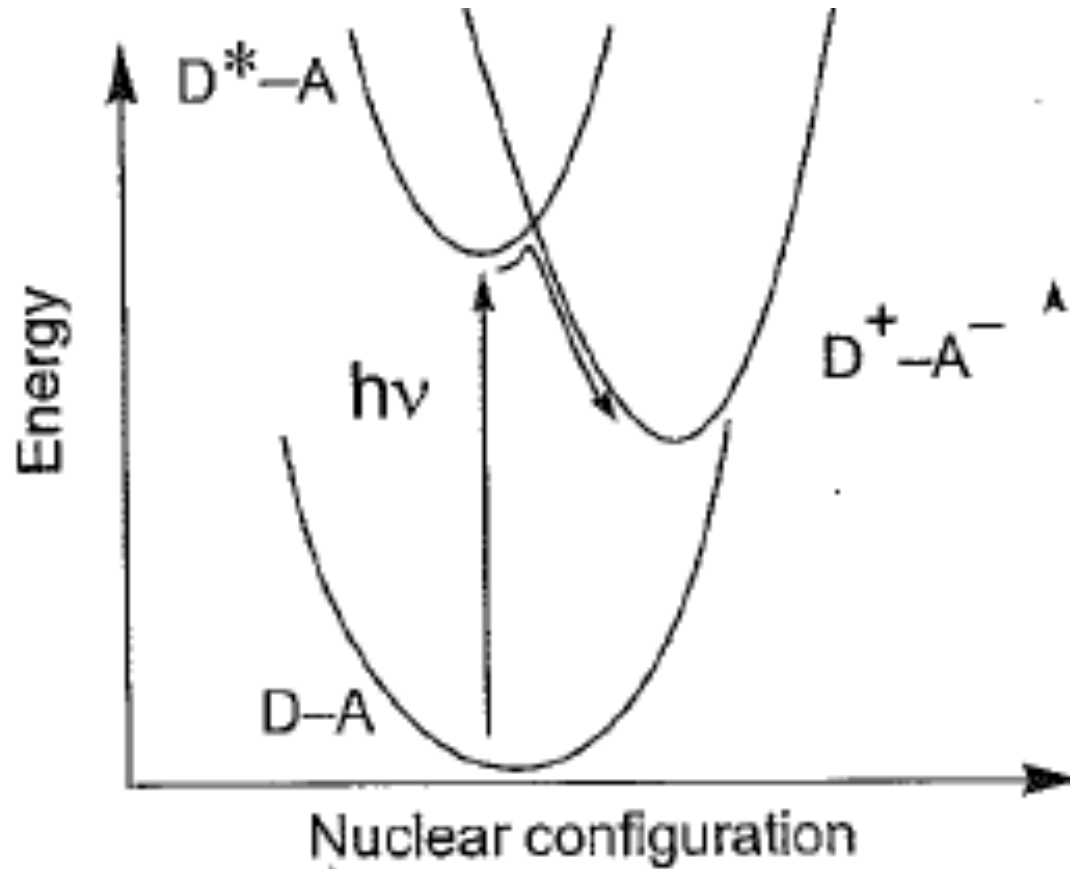
The Nobel Prize in Chemistry 1992

The Nobel Prize in Chemistry 1983 was awarded to Henry Taube "for his work on the mechanisms of electron transfer reactions, especially in metal complexes".
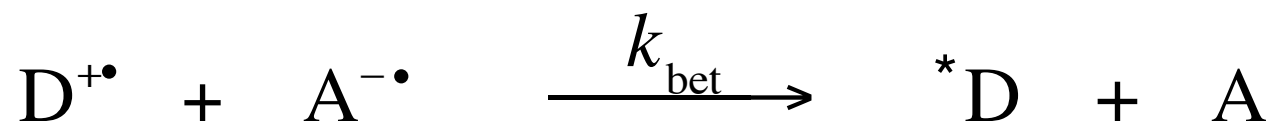
The Nobel Prize in Chemistry 1992 was awarded to Rudolph A. Marcus "for his contributions to the theory of electron transfer reactions in chemical systems".

Forward and back electron transfer

Chemiluminescent Electron Transfer

$$D^{+\bullet} \quad + \quad A^{-\bullet} \quad \xrightarrow{\quad k_{bet} \quad} \quad {}^{*}D \quad + \quad A$$

Two situations which can contribute to the formation of an excited state from an electron transfer between D^+ and A^- are:

When back electron transfer to the ground state ($D^{\bullet+} + A^{\bullet-} \to D + A$) is in the Marcus inverted region and is therefore inhibited; the formation of the excited products (e.g., $D^{\bullet+} + A^{\bullet-} \to {}^{*}D + A$) may be kinetically preferred because of the smaller ΔG^0_{et}

When a triplet radical ion pair undergoes back electron transfer, spin selection rules forbid the formation of D + A (singlet products), but allow the formation of an excited triplet state of D or A, i.e., when ${}^{3}(D^{\bullet+}, A^{\bullet--}) \to {}^{1}(D,A)$ is spin forbidden, while ${}^{3}(D^{\bullet+}, A^{\bullet-}) \to {}^{3}D, A$ is spin allowed

Excited state production through back electron transfer
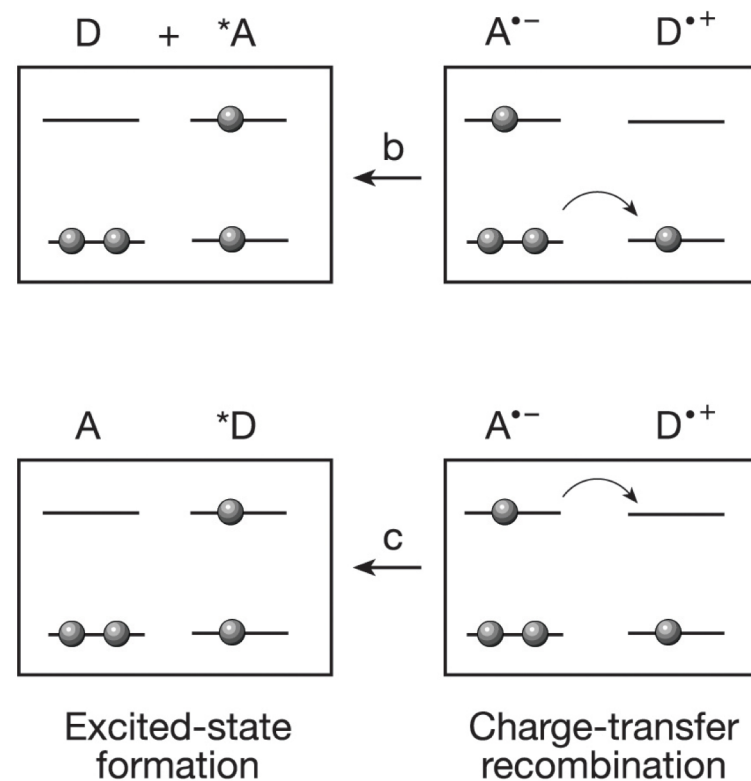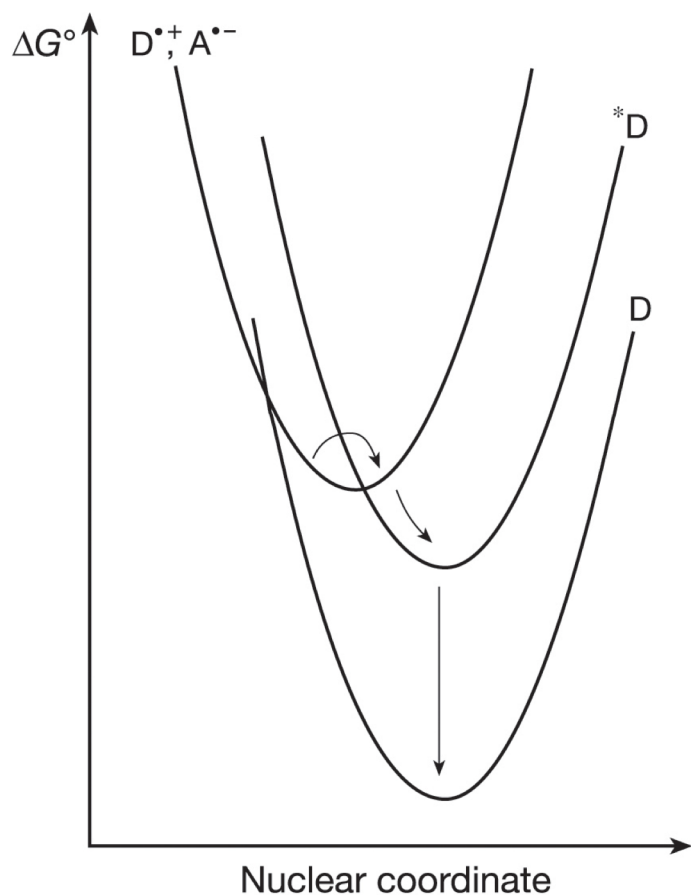
Bioapplications, Light emitting diodes (TV, Computer, Cell phone screens)