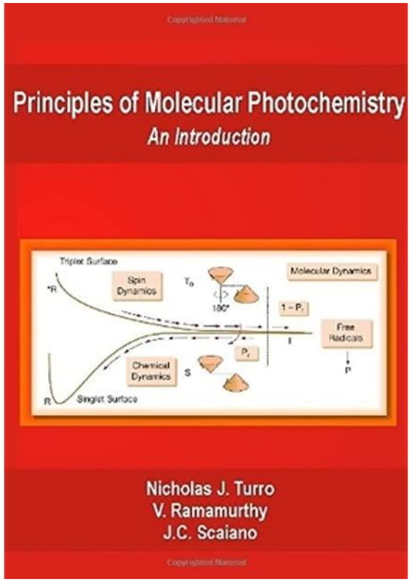
Chapter 7: Energy and Electron Transfer



CHEM 6420

Introduction to Energy and Electron Transfer

- The four cases below represent energy- and electron-transfer processes from *R to M (second molecular species)

1) Exchange electronic energy transfer, where *R is an energy donor, M is an energy acceptor. $^*R + M \rightarrow R + {}^*M$

2) Dipole–dipole electronic energy transfer, where *R is an energy donor, M is an energy acceptor, where $^*R + M \rightarrow R + {}^*M$

3) Electron transfer, where *R(D) behaves as an electron donor, M(A) behaves as an electron acceptor; $I(R^{\bullet +}, M^{\bullet -})$ is a radical ion pair (RIP). $^*R(D) + M(A) \rightarrow I(R^{\bullet +}, M^{\bullet -})$

4) Electron transfer, where *R(A) behaves as an electron acceptor, M(D) behaves as an electron donor; $I(R^{\bullet -}, M^{\bullet +})$ is RIP. $^*R(A) + M(D) \rightarrow I(R^{\bullet -}, M^{\bullet +})$

Introduction to Energy and Electron Transfer

- Cases 1 and 2 are *electronic energy-transfer processes*

- For case 1, the energy-transfer results from orbital overlap between *R and M; electron exchange occurs during orbital overlap and provides the interaction responsible for the energy-transfer event

- For case 2, energy-transfer results from the interaction of an *oscillating electric dipole field* that surrounds the space about *R and the electrons of M

- The critical difference between cases 1 and 2 is that dipole–dipole interactions of two electric fields and does not require orbital overlap

- Since it involves the interactions of fields, dipole–dipole interactions can occur through empty or molecularly occupied space

Introduction to Energy and Electron Transfer

- Cases 1 and 2 are therefore completely different interactions that will possess different rate constant dependencies on factors, such as the distance separation and optical properties of *R and M

- For energy-transfer processes, *R is always the energy donor and M is always the energy acceptor

Introduction to Energy and Electron Transfer

- Cases 3 and 4 are *electron-transfer processes*

- In an electron-transfer process, *R may be an electron donor (case 3) or acceptor (case 4)

- We use the symbol “D” to indicate when *R (or M) is an electron donor and the symbol “A” for electron acceptor

- For case 3, electron transfer is triggered by frontier orbital overlap interactions that result in electron transfer from the LU of *R(D) to the LU of M(A)

- For case 4, electron transfer is triggered by frontier orbital interactions that result in electron transfer from the HO of M(D) to the HO of *R(A)

Introduction to Energy and Electron Transfer

- Some of the most important parameters in photoinduced electron- and energy-transfer are the rate constant (*k*) of the primary photochemical process and the dependence on *k* on features, such as:

    - The distance separation between *R and M
    - Solvent polarity
    - The structure of *R and M
    - The electronic excitation energy possessed by *R
    - The redox potentials of *R and M

Introduction to Energy and Electron Transfer

- Let E_{*R} be the electronic excitation energy of R and E_{*M} be the electronic excitation energy of M
- The bimolecular rate constant (k) of the primary photochemical process *R + M → R + *M will depend strongly on whether the overall energy-transfer process is energetically downhill (termed *exothermic*, $E_{*R} > E_{*M}$) or uphill (termed *endothermic*, $E_{*R} < E_{*M}$)
- In fluid solution, an energy transfer process usually proceeds at a rapid rate, often close to the rate of diffusion, if the overall energy-transfer process *R + M → R + *M is exothermic (see Figure on the right)
- In order to conserve energy during the energy-transfer elementary step, since the electronic energy of *R is greater than that of *M, the energy transfer will require excitation of vibrations of *M (υ = 4 in the case on the right)

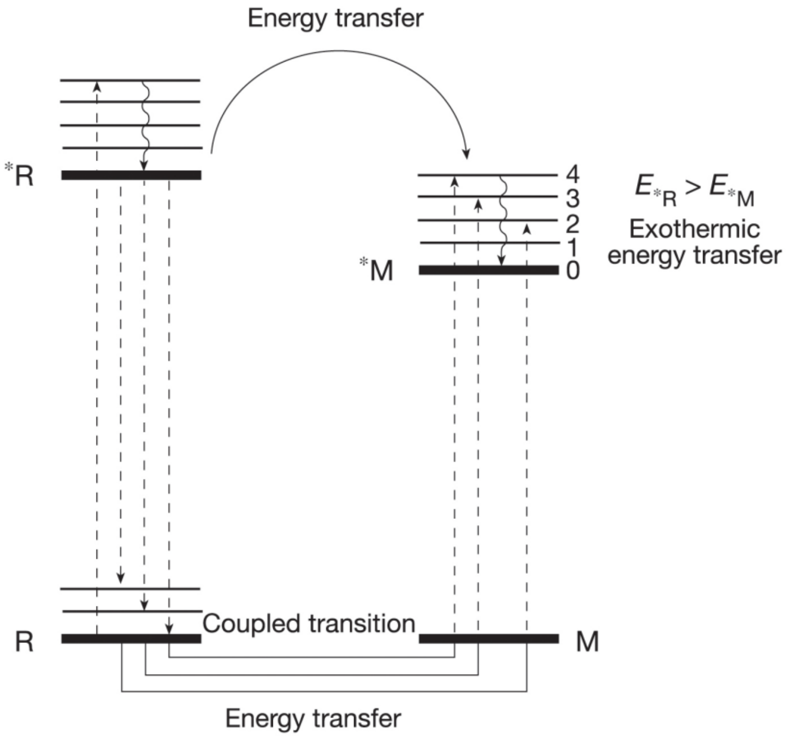


Figure 7.1 copyright 2009 University Science Books

Introduction to Energy and Electron Transfer

- Photoinduced electron transfer corresponds to a primary photochemical process, a *R → $I(RIP)_{gem}$ step for which I is a *geminate (gem) radical ion pair*

- The RIP that is produced by electron transfer is termed a “geminate pair” since the two partners of the RIP were *born together* (are gem) as the result of an electron-transfer event

- The rate constant (*k*) of the *electron-transfer* process is determined not only by the electronic excitation energy of *R, which can be employed to drive the electron-transfer process, but also by the thermodynamics of the electrochemical reduction–oxidation (redox) characteristics of the overall electron-transfer process

Introduction to Energy and Electron Transfer

- In solution, the rates and efficiencies of energy and electron-transfer processes will depend not only on electronic and energetic factors but also on key mechanical processes related to molecular diffusion:

1) The diffusional process that bring the reactants (*R and M) together to within a critical distance (r_c) at which energy or electron transfer can occur in competition with deactivation of *R

2) The relative competition between reaction and nonreactive separation of reactants after the critical distance (r_c) has been achieved

3) The successful or unsuccessful irreversible separation of the primary products produced by either energy or electron transfer

Introduction to Energy and Electron Transfer

- The diffusion of *R and M from random initial positions in liquid to form a collision pair in a solvent cage is characterized by a rate constant for diffusion (k_{dif})
- The latter is a very important solvent-dependent quantity since k_{dif} determines the limiting rate at which *R and M can be delivered as colliding partners in a solvent cage
- k_{dif} can be readily estimated for liquids from their viscosities using a simplified expression known as the Debye equation (eq 1):

$$k_{dif} = \frac{8RT}{3000\eta} \qquad (1)$$

where η is the viscosity of the solvent (in units of Poise, P), T is the temperature, and R is the gas constant (1.987 cal mol^{-1} K^{-1})

- For typical non-viscous organic solvents (benzene, acetonitrile, hexane) at room temperature, η is ~ 1-10 cP, making k_{dif} for non-viscous solvents in the range of $10^9 – 10^{10}$ M^{-1} s^{-1}
- This is the benchmark for diffusional processes in fluid solution, since it represents *the fastest rate at which electron and energy transfer that require substantial orbital overlap can occur*

The Electron Exchange Interaction for Energy and Electron Transfer

- Energy- and electron-transfer reactions (induced by electron exchange interactions) will be covered jointly and comparatively to emphasize conceptual similarities and equivalence of the two processes in terms of orbital interactions

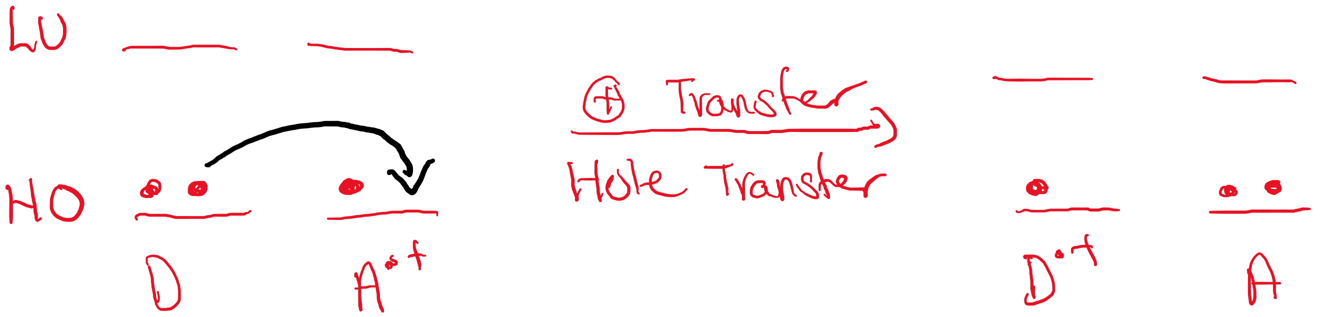
- Let's now examine the basic orbital interactions that relate these two *electron exchange* processes from the point of frontier orbital (HO and LU) representations

- In the physics literature, a half-filled HO is considered a "positive hole" in the electronic framework of a molecule

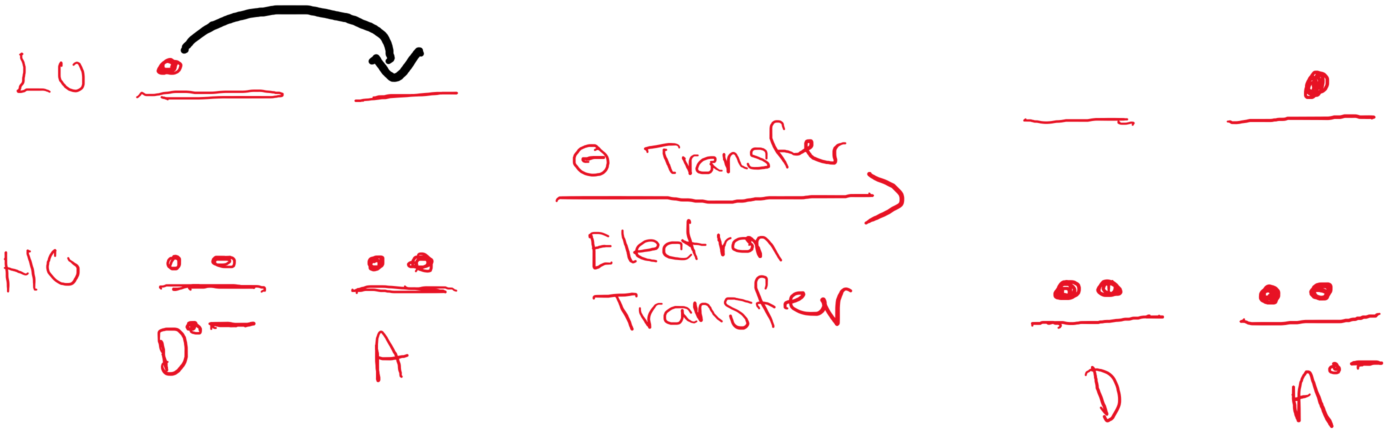
- *R is viewed as simultaneously possessing both a positive hole (one electron in the half-filled HO) and one electron in the half-filled LU
  - Physicists *R an *exciton*

The Electron Exchange Interaction for Energy and Electron Transfer

- The figure below represents a "positive-hole transfer", where a half-filled HO is moved from one molecule to another
  - Can also be viewed as electron-transfer from D to $A^{\bullet+}$

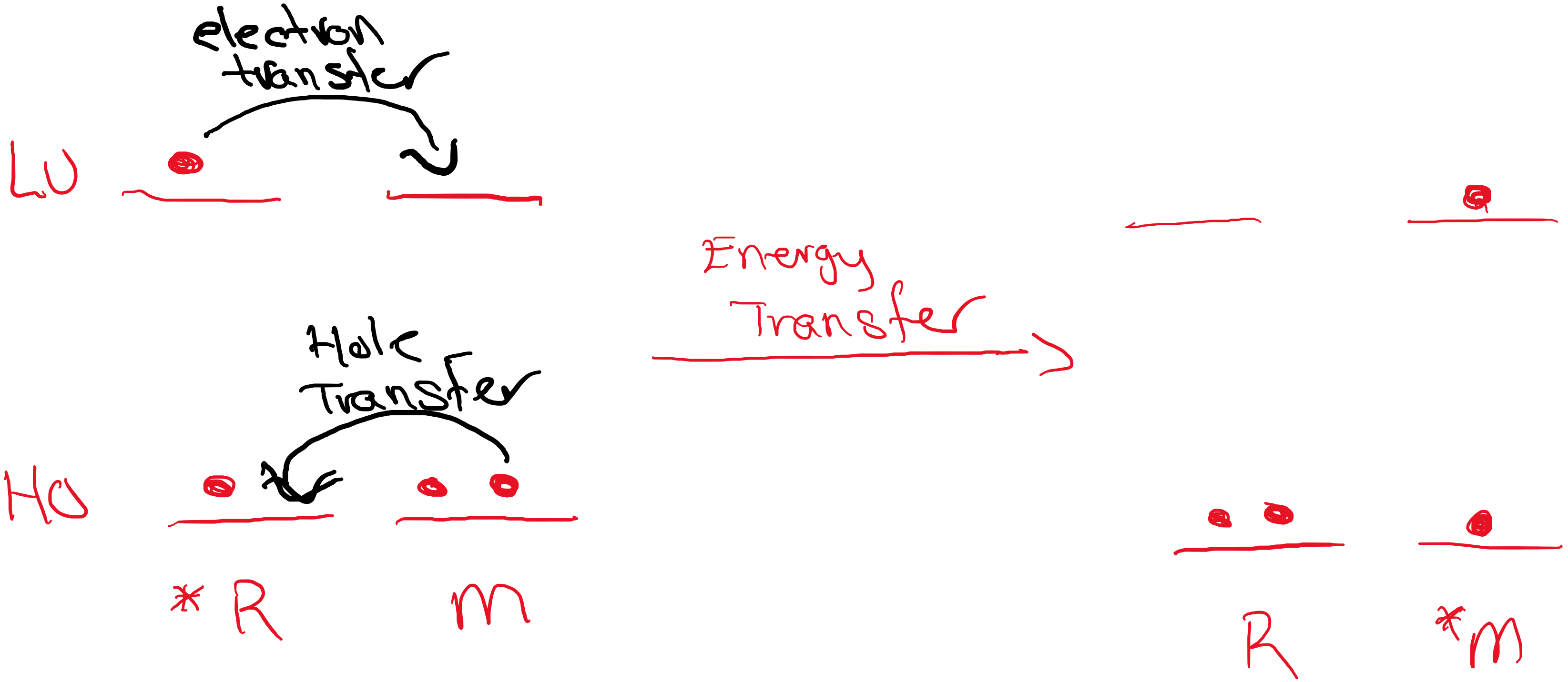


- The figure below represents an electron-transfer process, where an electron is transferred from one half-filled LU to another



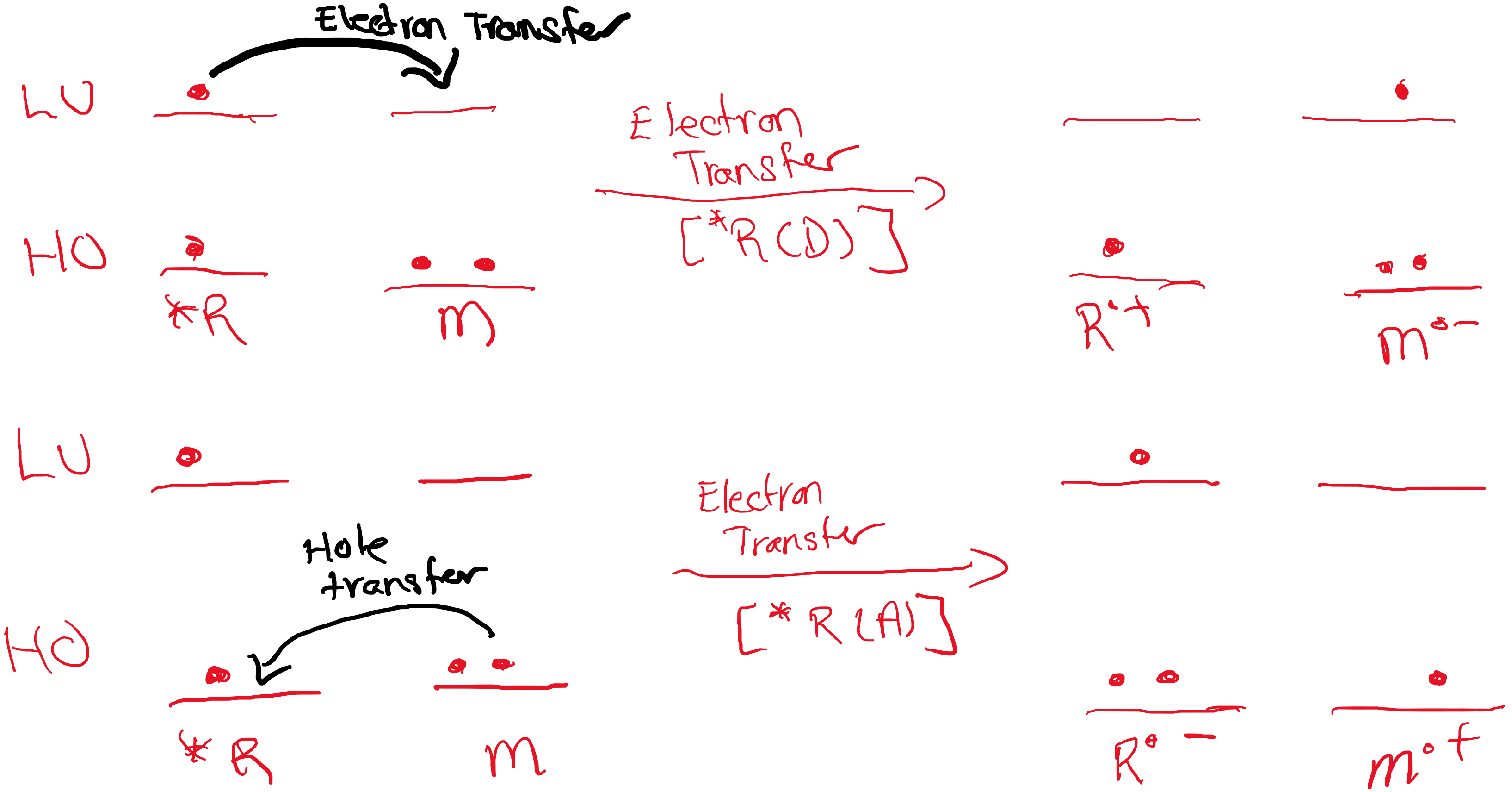
The Electron Exchange Interaction for Energy and Electron Transfer

- Now let's examine energy-transfer, which can be viewed as the sum of a synchronous (negative) electron- and (positive) hole-transfer process



The Electron Exchange Interaction for Energy and Electron Transfer

- Since an electronically excited state (*R) simultaneously possesses a half-filled HO and a half-filled LU, *R *may serve as either an electron donor or an electron acceptor*
- Whether *R will serve as an electron donor or acceptor will depend on factors that determine the exothermicity of the overall electron-transfer process (that is, the electron-accepting or donating ability of M)



The Electron Exchange Interaction for Energy and Electron Transfer

- Photochemical and photophysical processes of *R are always potentially available to compete with the primary processes of energy or electron transfer
- Eq 2-5 illustrate steps that can plausibly be competitive with energy-transfer between an excited donor (*D) and acceptor (A)

$$^{*}D \xrightarrow{k_D} D\ (+\ h\nu\ or\ \Delta) \tag{2}$$

$$^{*}D + A \xrightarrow{k_{ET}} D + \ ^{*}A \tag{3}$$

Typically lost to solvent

$$^{*}D + A \xrightarrow{k_W} D + A \tag{4}$$

Electron-transfer

$$^{*}D + A \xrightarrow{k_{rxn}} Chemical\ Change \tag{5}$$

The Electron Exchange Interaction for Energy and Electron Transfer

- Eq 2 represents all the *unimolecular photophysical processes* of radiationless or radiative deactivation of *D to D, which are grouped together with the rate constant k_D

- Eq 3 specially represents the energy-transfer (ET) step of interest with rate constant k_{ET}

- Eq 4 represents all "*energy-wasting* (W) *steps*" in which bimolecular interaction of *D to A cause "nonreactive quenching" of *D to D with a bimolecular rate constant (k_W)

- Eq 5 represents all primary photochemical reactions of *D and A with a bimolecular rate constant k_{rxn}

The Electron Exchange Interaction for Energy and Electron Transfer

- Note that of all the processes available to *D, <u>only eq 3 leads to energy transfer</u> (denoted ET; electron-transfer: et)

- Therefore, if we determine an experimental rate constant (k_q) for "total bimolecular quenching" of *D by A, the value of k_q will incorporate ***all modes of bimolecular deactivation*** (eq 3-5) of *D by A as shown in eq 6:

$$k_q = k_{ET} + k_W + k_{rxn} \tag{6}$$

- If we measure an experimental rate constant for decay of *D in the presence of A, k_{exp} is a measure of all the overall unimolecular (k_D) and bimolecular (k_q) processes available to *D given by eq 7:

$$k_{exp} = k_D + k_q[A] \tag{7}$$

The Electron Exchange Interaction for Energy and Electron Transfer

- The *quantum efficiency* (ϕ_{ET}) corresponds to the fraction of *D molecules that decay via energy transfer (eq 8)

$$\phi_{ET} = \frac{k_{ET}[A]}{k_D + k_q[A]} \tag{8}$$

- The *quantum efficiency* (ϕ_{ET}) differs from the *quantum yield* of energy transfer (Φ_{ET}) in that Φ_{ET} accounts for the efficiency in which *D is formed (eq 9)

$$\Phi_{ET} = \Phi_{^*D}\phi_{ET} \tag{9}$$

Note: Φ_{*D} may be the quantum yield of ISC (Φ_{ISC}) in the case of triplets

“Trivial” Mechanism for Energy and Electron Transfer

- Curiously, there exists energy- and electron-transfer processes that occur when there is no electronic interaction (no electron exchange or dipole–dipole interactions) between *D and A!

- How? There exists “trivial” mechanisms for energy and electron transfer

- In the trivial mechanism for energy transfer, *R emits a photon (fluorescence or phosphorescence) that is subsequently absorbed by M to produce *M

- In the trivial mechanism for electron transfer, *R can eject an electron (photoionization) that is subsequently attached to M to produce $M^{\bullet -}$

“Trivial” Mechanism for Energy and Electron Transfer

- A *trivial* or *radiative* emission–absorption energy transfer mechanism consists of the emission of light by the excited donor (*D) followed by the absorption of the emitted photon by a ground-state acceptor (A)

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

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

- For energy transfer that occurs by electron exchange or dipole–dipole interactions, the lifetime of *D is always decreased as the result of the bimolecular interaction

- For the trivial mechanism of energy transfer, the acceptor does not at all influence the emission lifetime or probability of *D

- Instead, if the acceptor A, if it happens to be in the path of the photon, merely intercepts the photon *after* it has been emitted by *D

“Trivial” Mechanism for Energy and Electron Transfer

- Since “trivial” mechanisms for energy transfer require that *D emits a photon that A is capable of absorbing, <u>the emission spectrum of *D must overlap with the absorption spectrum of A</u>
- The rate or probability per unit time of energy transfer from *D to produce *A by a trivial mechanism will depend on numerous factors:

1) The quantum yield for emission of *D
2) The number of molecules (concentration) in the path of photons emitted by *D
3) The light absorbing ability of A
4) The overlap of the emission spectrum of *D and the absorption spectrum of A, with consideration to the extinction coefficient of A at the wavelength of overlap

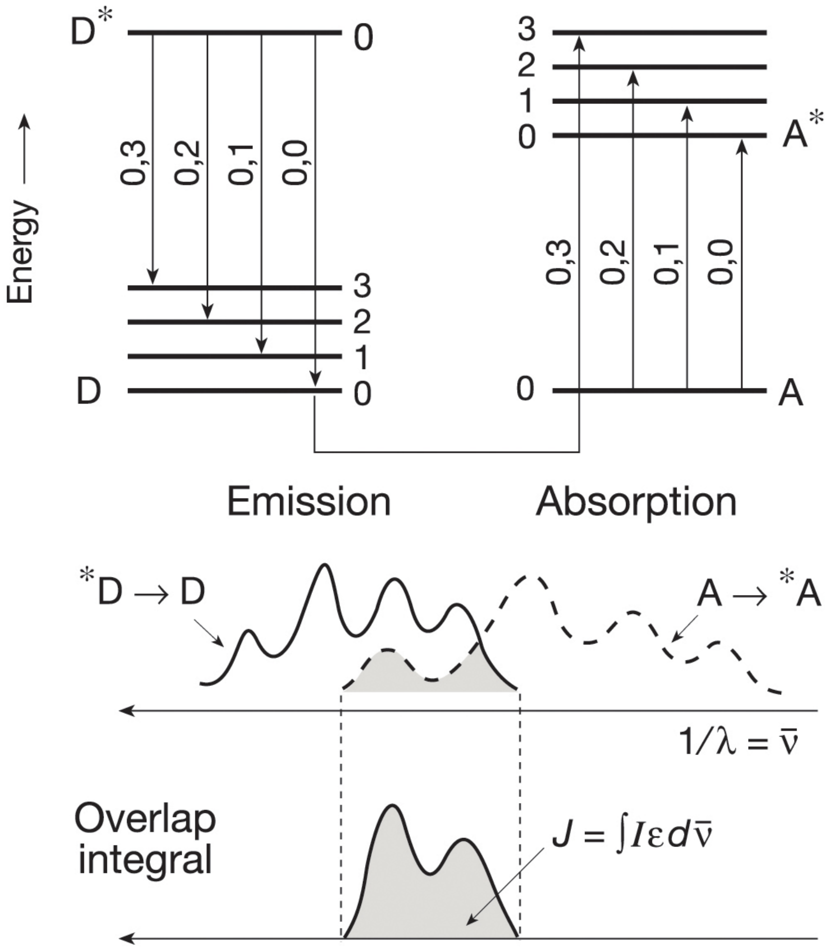


Figure 7.3 copyright 2009 University Science Books

“Trivial” Mechanism for Energy and Electron Transfer

- The simple two-step mechanism for trivial electron transfer is shown below:

$$D + h\nu \rightarrow {}^{*}D \rightarrow D^{\bullet +} + e^{\bullet -}_{solv} \tag{10}$$

$$e^{\bullet -}_{solv} + A \rightarrow A^{\bullet -} \tag{11}$$

- In this case, the “emitted” species is an electron, which immediately becomes surrounded by solvent to yield a “solvated electron” ($e^{\bullet -}_{solv}$)
- The electron is then “absorbed” by a suitable acceptor to form a radical anion ($A^{\bullet -}$)
- Eq 10 is the primary photochemical process termed *photoionization*, which may involve a transient excited state (*D)
- Nearly all molecules undergo photoionization when they absorb a photon whose energy (E = hν) exceeds the ionization potential of a molecule in solution
- Lasers can produce very high [photons] that are absorbed by D. The [photons] can be so high that *D can then absorb a second photon to cause photoionization

Energy Transfer Mechanisms

- As previously described, the most commonly encountered electronic energy transfer processes take place by two distinct types of electronic interactions between *D and A:

1) Exchange electronic energy transfer, where *R is an energy donor, M is an energy acceptor. *R + M → R + *M
   - Referred to as Dexter Energy Transfer
   - Interaction between *D and A is made through *the overlap of orbitals of* *D *and* A

2) Dipole–dipole electronic energy transfer, where *R is an energy donor, M is an energy acceptor, where *R + M → R + *M
   - Referred to as Förster Energy Transfer
   - Interaction between *D and A is made through space by *the overlap of the dipolar electric fields of* *D *and* A

Energy Transfer Mechanisms

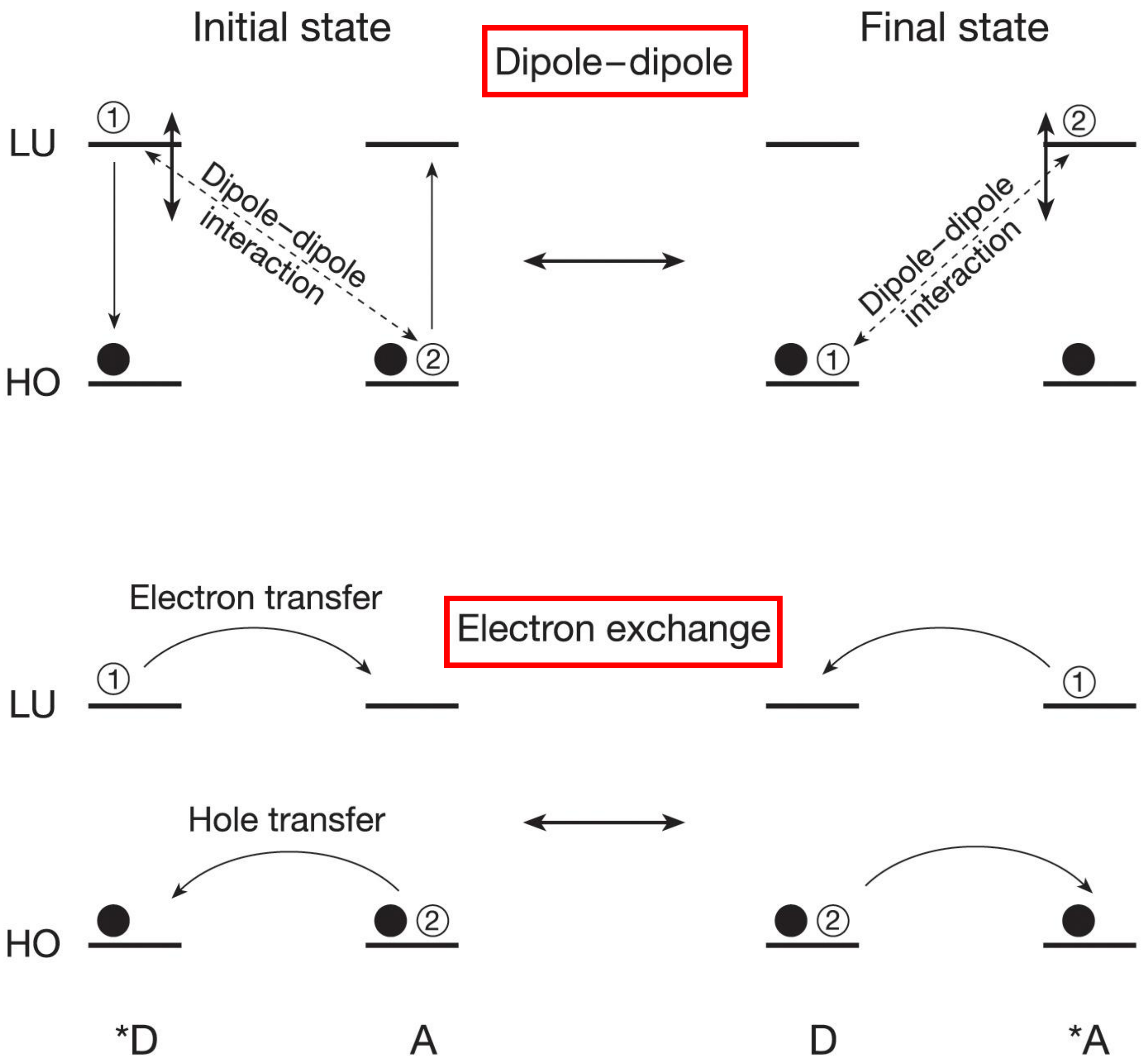


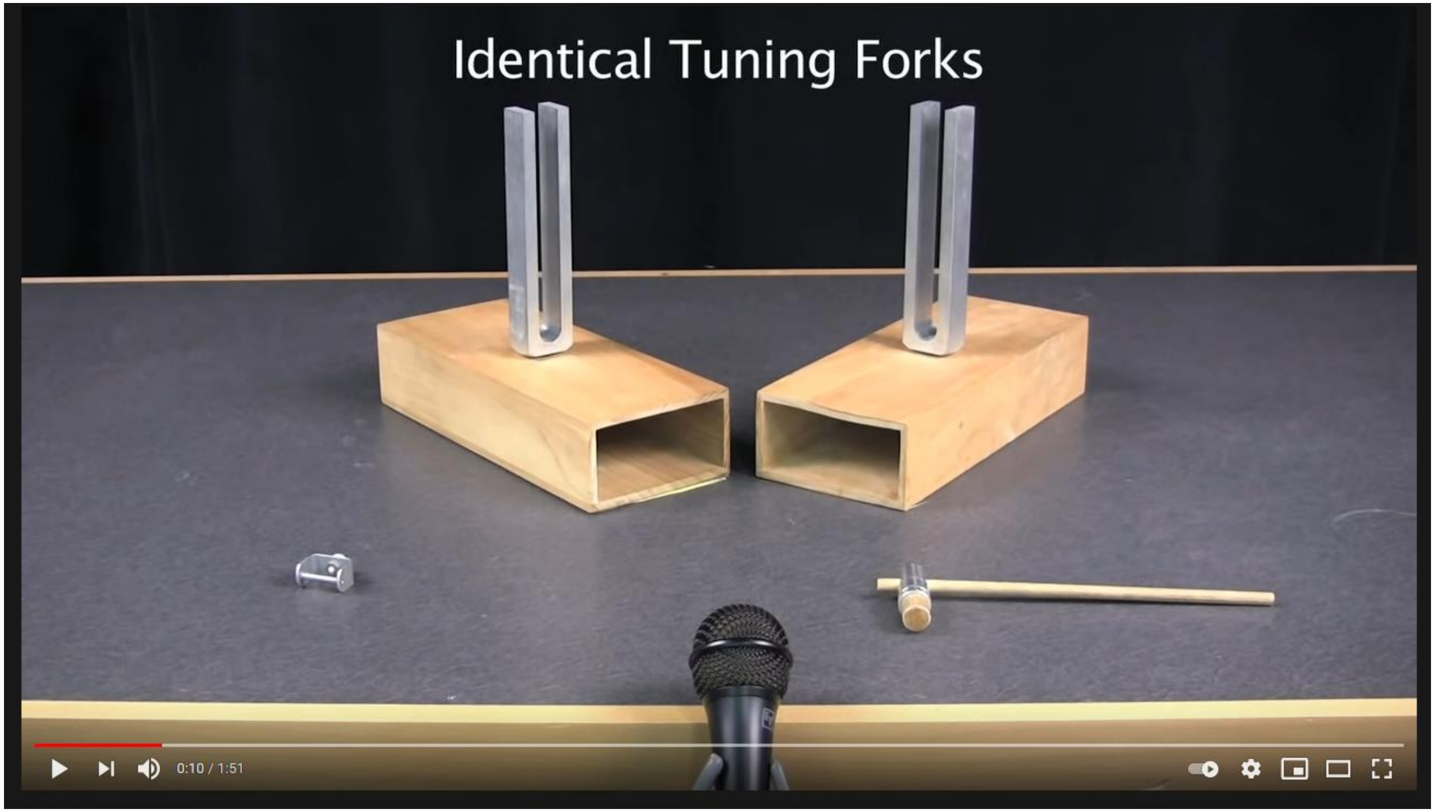
Figure 7.4 copyright 2009 University Science Books

Energy Transfer Mechanisms

How can we visualize Förster Energy Transfer?

We can use tuning forks as an analogy

https://www.youtube.com/watch?v=aCocQa2Bcuc



Energy Transfer Mechanisms

- From the classical theory of electromagnetic radiation that views all the electrons of a molecule as being harmonic oscillators that can undergo oscillation
- *An electron in the ground state of the harmonic oscillator does not oscillate at all*
- However, *D possesses an excited electron, which corresponds to the excited state of a harmonic oscillator
- For any excited state of a harmonic oscillator, *the electron undergoes periodic harmonic oscillations along the molecular framework with a certain natural frequency* (ν_0)
- Such oscillations create an oscillating dipole
- Therefore, *D (but not A) is imagined to possess an oscillating electric dipole that, in turn, produces an oscillating electric field in the space around *D

Energy Transfer Mechanisms

- The effect of an oscillating electric field of *D on a nearby A can be visualized

- In classical theory, A can be visualized as being an initially non-oscillating electric receiver that is potentially capable of being driven into resonance by the oscillating electric field of the transmitting antenna *D

- Suppose the frequency ν_0 at which the electron of *D oscillates matches a natural frequency for A oscillation (first required condition)

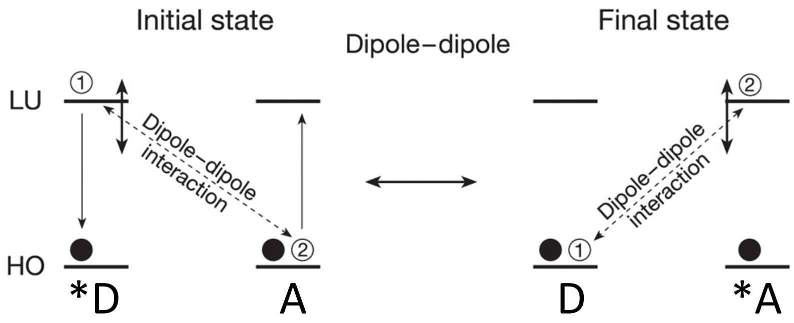
- If the oscillating electric field of *D is of sufficient strength and close enough to A to interact with A to induce oscillations, the conditions for classical resonance and dipole–dipole energy transfer from *D to A are met

Energy Transfer Mechanisms

- From this classical model, *the energy transfer requires the existence of a common frequency of oscillation (ν_0) for *D and A*

- When this condition is met, the efficiency of the energy transfer will be determined mainly by:
  - The distance of separation (R_{DA}) of *D and A
  - The ease at which A can be set into oscillation for the common frequency
  - The relative orientation of *D and A

Energy Transfer Mechanisms



- For dipole–dipole energy transfer, electrons do not “exchange molecules or orbitals”, but rather two transitions (*D → D and A → *A) occur simultaneously as resonance by which the oscillating electric field of *D triggers the creation of a coupled oscillating dipole field about A and leads to *A
    - Oscillating dipoles represented by ↕

- The excitation of A to *A by the dipole–dipole mechanism is analogous to the mechanism for the absorption of light described in Chapter 4

- The oscillating electric field of *D thus serves as a “virtual photon” for the production of *A

Visualization of ET by Dipole–Dipole Interactions

- This dipole–dipole coupling mechanism of energy transfer is plausible only in multiplicity–conserving (spin-allowed) transitions that have large transition dipoles (μ)

- Only singlet–singlet transitions have large oscillator strengths and are associated with large transition dipoles

- Therefore, *only singlet–singlet energy transfer is generally plausible by the dipole–dipole mechanism*

- However, we will see later that electron exchange provides an effective mechanism for triplet–triplet energy transfer

Visualization of ET by Dipole–Dipole Interactions

- For the radiative transition A + hν → *A, the resonance condition (energy of transition is equal to the energy for a photon of frequency, ν) is given by:

$$\Delta E(\mathrm{A} \rightarrow {}^*\mathrm{A}) = h\nu$$

- As a reminder, *energy conservation is an absolute requirement for energy transfer by any mechanism*
- For molecules, matching *D → D and A → *A transitions will generally involve matching of vibrational energy levels
- Since *D will be in its lowest vibrational level ($\upsilon = 0$), we see that an excited vibrational level of *A will be produced in the energy transfer process

$$\Delta E({}^*\mathrm{D} \rightarrow \mathrm{D}) = \Delta E(\mathrm{A} \rightarrow {}^*\mathrm{A})$$

- Since the resonance condition must be met, we can deduce a common frequency of oscillation, since $\Delta E = h\nu$ so $\nu = \Delta E/h$

The Förster Theory of Dipole–Dipole ET

- As shown in eq 2, the electrostatic interaction energy (*E*) between two electric dipoles is directly related to the magnitude of the two interacting dipoles (μ_D and μ_A), and inversely related to the cube of the distance between the donor and the acceptor (R_{DA})

$$E(dipole - dipole)\ \alpha\ \frac{\mu_D \mu_A}{R_{DA}^3} \tag{2}$$

- Förster related the electric dipoles (μ_D and μ_A) to the oscillator strengths (f_D and f_A) for radiative *D ↔ D and A ↔ *A transitions, respectively

- The theoretical quantities f_D and f_A are related to the experimental extinction coefficients ε_D and ε_A

- *We can now see how factors that control the strengths of electronic radiative transitions also control the strength of dipole interactions in dipole–dipole energy transfer at a fixed* R_{DA}

The Förster Theory of Dipole–Dipole ET

- The magnitude of the rate of energy transfer (k_{ET}) is proportional to the square of the interaction energy (E), as shown in eq 3:

$$k_{ET}\ \alpha\ E^2\ \alpha\ \frac{\mu_D^2 \mu_A^2}{R_{DA}^6} \qquad (3)$$

- Note that the k_{ET} is expected to fall off as the separation (R_{DA}) between *D and A increases, by a factor of $1/R_{DA}^6$

This $1/R_{DA}^6$ distance dependence, when it can be measured accurately, is a basis for distinguishing energy transfer that occurs by dipole–dipole interactions from electron exchange interactions, since the latter generally falls off exponentially with separation R_{DA}

The Förster Theory of Dipole–Dipole ET

- The following plot compares the dependence on k_{ET} by the dipole–dipole and by the electron exchange mechanisms, where the falloff of ln k_{ET} compared to the deactivation of the donor (k_D) is given as a function of separation of *D and A
- At small separations (< 10 Å) for both interactions, $k_{ET} >> k_D$ (very efficient)
- For values of R_{DA} > 10 Å, the falloff of k_{ET} by the exchange mechanism is generally steeper than the $1/R^6$ falloff of the dipole-dipole interaction
- Even at R_{DA} ~30 – 40 Å, k_{ET} for dipole-dipole energy transfer is still competitive with k_D

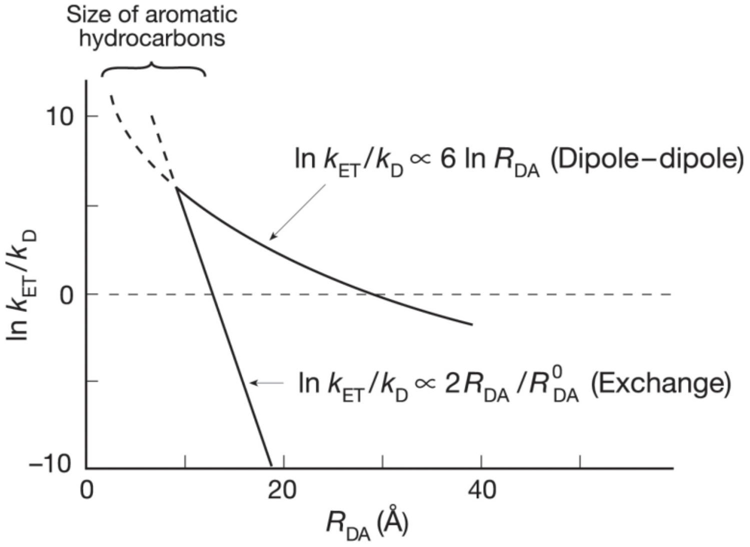
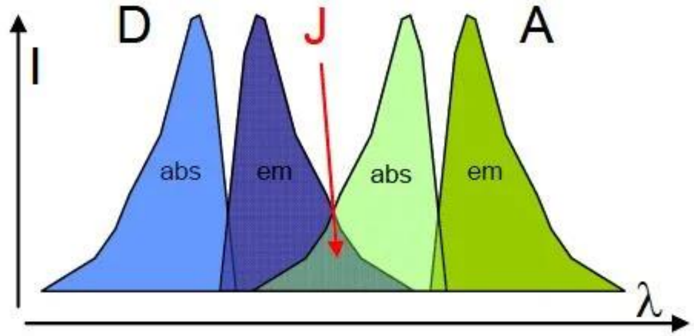


Figure 7.5 copyright 2009 University Science Books

Relationship of k_{ET} to Energy-Transfer Efficiency

The rate constants of energy transfer (k_{ET}) induced by a Förster energy transfer mechanism will be maximal when:

1) The D* → D and A → *A transitions correspond to a large spectral overlap integral, *J*. A larger value of *J* means that there are many resonant *D → D and A → *A transitions



2) The radiative rate constant (k_D^0) is as large as possible
   - A large value of k_D^0 means that the *D → D transition possesses a large oscillator strength (*f*), which means that the size of the oscillating transition dipole (μ_D) due to the excited electron in *D is very large and is a strong oscillator

Image from https://www.azom.com/article.aspx?ArticleID=10458

Relationship of k_{ET} to Energy-Transfer Efficiency

The rate constants of energy transfer (k_{ET}) induced by a Förster energy transfer mechanism will be maximal when:

3) The magnitude of ε_A is as large as possible in the overlap region
   - A larger value of ε_A means that the A → *A transition possesses a large oscillator strength (*f*), which in turn means that the size of the oscillating dipole (μ_A) is large

4) The spatial separation (R_{DA}) between *D and A is smaller than the critical separation required for efficient energy transfer
   - The closer *D is to A, the stronger is its oscillating force field felt by A, and therefore the more powerful its interaction with A

5) For a given separation for which *D is interacting with A, there will be preferred relative orientations of *D and A for which energy transfer is favorable and fast
   - See next slide

Orientation Dependence of the Energy of Interacting Dipoles

From Chapter 2 of the text:

- Eq 4 refers to the interaction of two point dipoles:

$$E(dipole - dipole) = \left[\left(\mu_D \mu_A / R_{DA}^3\right)\right](3\cos^2\theta - 1) \qquad (4)$$

- Near the "magic angles" of θ ~ 54° and 144°, *the dipole–dipole interaction is ~ 0*, i.e., for these angles of orientation, the dipolar interaction disappears even when *D and A are close in space and have large μ_D and μ_A, respectively

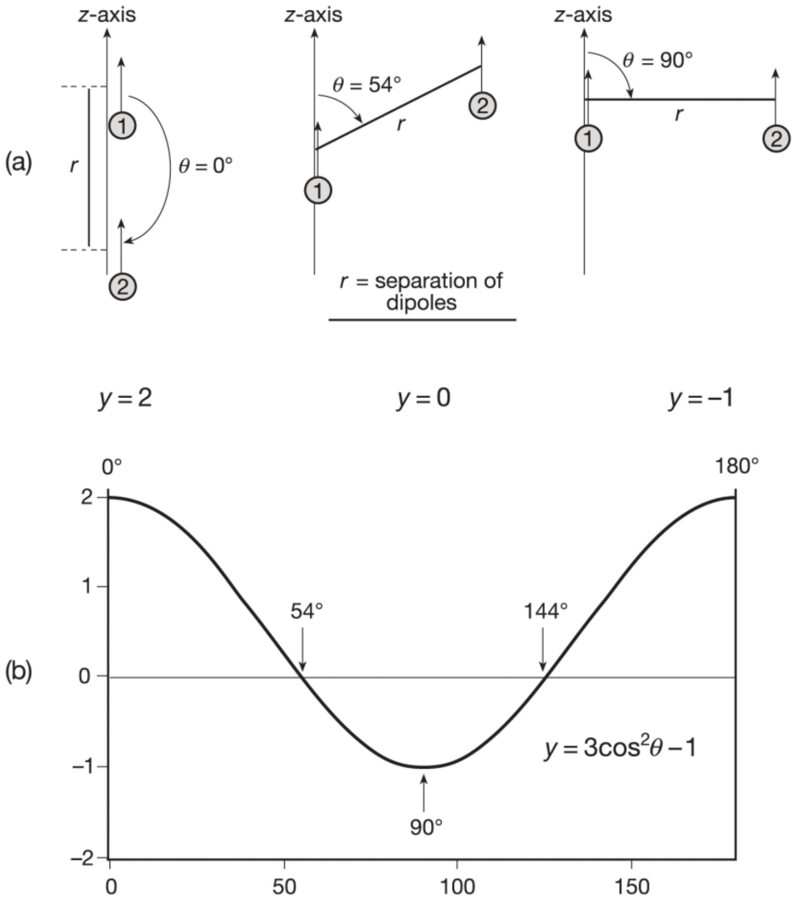


Figure 2.17 copyright 2009 University Science Books

Relationship of k_{ET} to Energy-Transfer Efficiency

- Experimentally, it is more convenient to measure the *efficiency of energy transfer* (ϕ_{ET}) rather than k_{ET} since ϕ_{ET} depends only on the spatial separation of *D and A
- It is convenient to define a separation R_{DA} for which the rate of energy transfer equals the sum of the rates of deactivation of *D, as shown in eq 5a and 5b

$$k_{ET}[\,^*D][A] = k_D[\,^*D] \;\; at \;\; R_{DA} = R_{DA}^0 \qquad (5a)$$

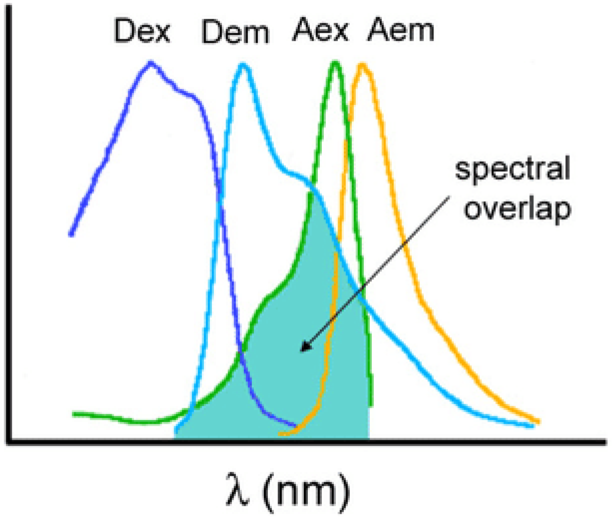
$$k_{ET}[A] = k_D = \tau_D^{-1} \qquad (5b)$$

- The distance at which 5a is valid is termed the "*critical separation distance*" (R_{DA}^0)
- When $R_{DA} < R_{DA}^0$, most of *D will deactivate by energy transfer, and when $R_{DA} > R_{DA}^0$ energy transfer becomes inefficient
- Therefore, the efficiency of energy transfer by dipole–dipole interactions may be related to the actual separation R_{DA} of *D and A by eq 6:

$$\phi_{ET} \;\alpha\; \left(\frac{R_{DA}^0}{R_{DA}}\right)^6 \qquad (6)$$

Relationship of k_{ET} to Energy-Transfer Efficiency

- Förster resonance energy transfer (commonly termed FRET) is widely used in photobiology as a ruler to determine distances between chromophores, sometimes strategically placed to examine special features or conformations of molecules



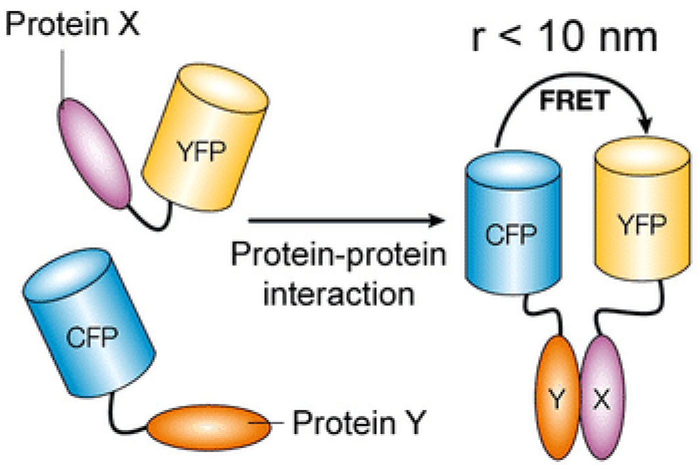
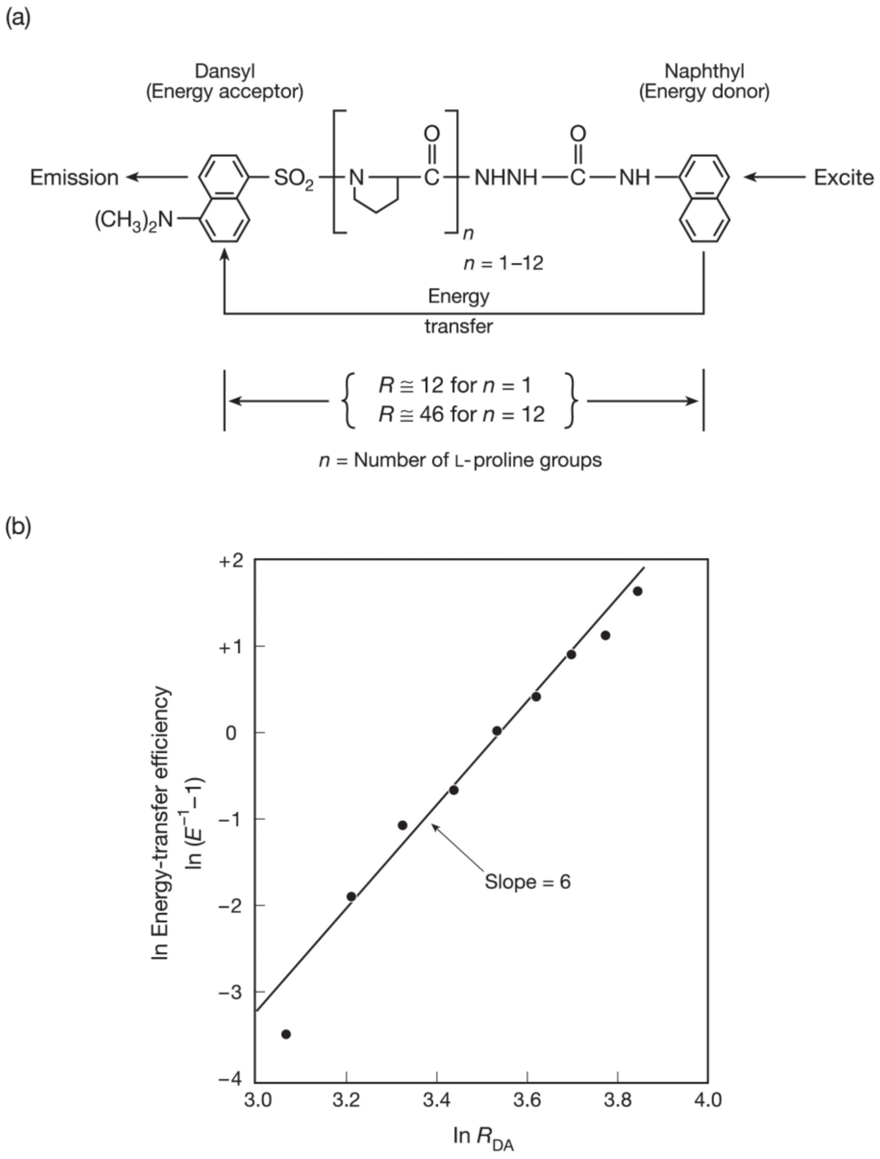


Image from ResearchGate

Experimental Tests for Dipole–Dipole ET

- An example of the dependence of FRET on distance is given by the results from a series of poly-L-proline oligomers
- In the series, the donor group (naphthyl) and the amino-separated acceptor group (dansyl) were separated by distances from 12 (for n = 1) to 46 Å (for n = 12)
- FRET was 100% efficient for $n \leq 4$, but the efficiency systematically drops as n (and R_{DA}) increases
- A ln – ln plot of eq 6 yields a slope of 6, the latter corresponds to the exponent for distance separation predicted by eq 6



Scheme 7.4 copyright 2009 University Science Books

Electron Exchange Processes

- Bimolecular chemical interactions are usually viewed as occurring via *collisions* between molecular reaction partners

- By collisions, it is meant that the participants in the reaction are sufficiently close that their electron clouds overlap significantly

- In any region of orbital overlap, electron exchange always occurs

- The following processes of interest to photochemists can result from electron exchange interactions produced by molecular collisions
  1) Triplet-triplet energy transfer
  2) Singlet-singlet energy transfer
  3) Triplet-triplet annihilation
  4) Electron transfer

An Orbital Overlap or Collision Mechanism of ET

Dipole–dipole interactions and electron exchange energy-transfer processes have the following differences in their characteristics:

1) The rate of dipole-induced energy transfer decreases as $1/R_{DA}^{6}$, whereas the rate of exchange-induced energy transfer decreases as exp(− R_{DA}/ R_{DA}^{0})
2) The rate of dipole-induced energy transfer depends on the extinction coefficient (ε) of the *D → D and A → *A radiative transitions, but the rate of exchange-induced energy transfer is independent of the extinction coefficients of the *D → D and A → *A transitions
3) The efficiency of energy transfer (fractions of transfers per donor lifetime ~ k_{ET}/k_D) by the dipole mechanism depends mainly on the oscillator strength of the A → *A transition and is directly related to the quantum yield of emission of *D, whereas the efficiency of energy transfer by the exchange interaction cannot be as directly related to experimental quantities
4) Both Förster and Dexter theories predict a dependence of k_{ET} on the spectral overlap integral (*J*), but only the Förster theory is dependent on the extinction coefficient of A → *A

Triplet–Triplet Annihilation

- The energy gap between the lowest triplet state (T_1) of a molecule and its ground state (S_0) is generally larger than the energy gap between the lowest singlet excited state (S_1) and the lowest triplet state (T_1)

$$\Delta E_{T_1-S_0} > \Delta E_{S_1-T_1} \qquad (7)$$

- If eq 7 is valid for a given system, when two triplets encounter generally there will be enough electronic excitation energy (2 X $\Delta E_{T_1-S_0}$) available to promote one of the two molecules into an excited singlet state (S_1), provided the second molecule relaxes to the ground state (S_0)

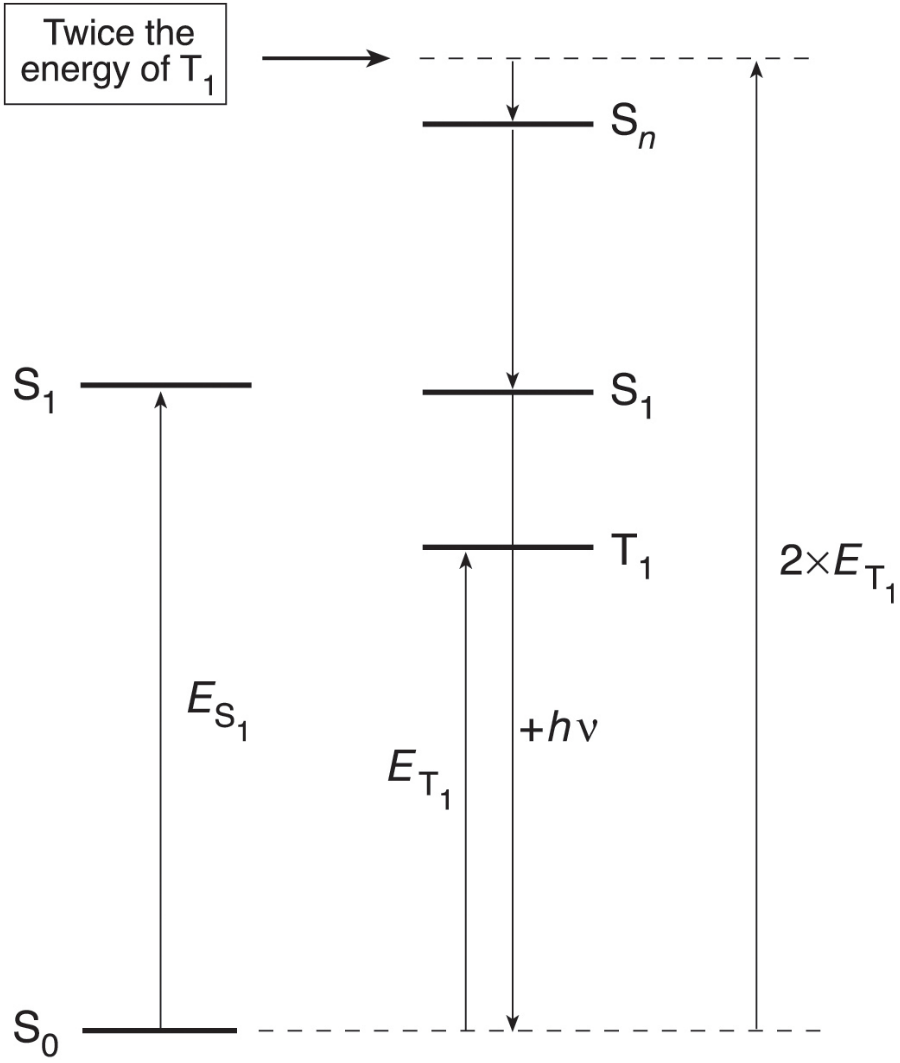


Figure 7.6 copyright 2009 University Science Books

Triplet–Triplet Annihilation

- Eq 8 represents the case where two triplet molecules are derived from the same ground state molecule

$$^*D(T_1) + \ ^*D(T_1) \xrightarrow{k_{TTA}} \ ^*D(S_1) + D(S_0) \quad with \quad \Delta H < 0 \qquad (8)$$

- This reaction where two triplets interact to produce an excited singlet state and a ground-state singlet is termed a *triplet–triplet annihilation*

- The figure below is a pictorial representation of electron exchange interactions in triplet–triplet annihilation leading to $^*D(S_1) + D(S_0)$

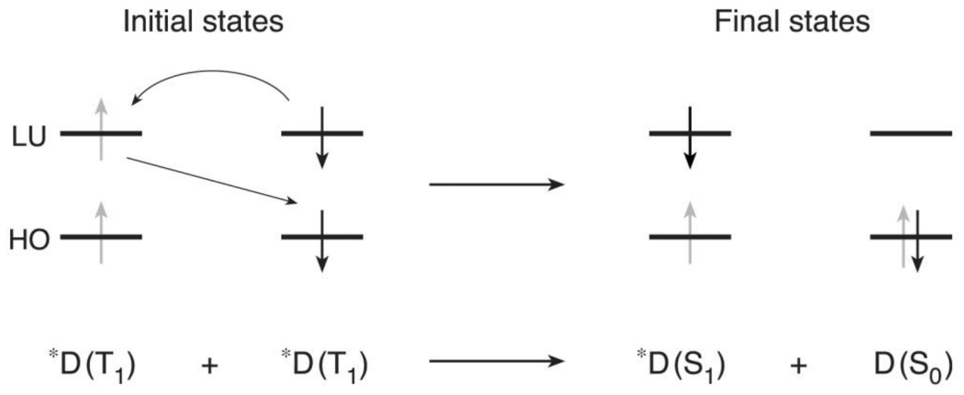


Figure 7.7 copyright 2009 University Science Books

Triplet–Triplet Annihilation

- If *D(S_1), produced by TTA, fluoresces with measurable efficiency, the result is *long-lived fluorescence*

- Although *D(S_1) itself has a very short lifetime, according to eq 8, this state is populated via *D(T_1), which has a relatively long lifetime

- Therefore, the concentration of *D(S_1) will continue to be replenished as long as *D(T_1) is present

- The *apparent* lifetime of this long-lived fluorescence will be on the order of the triple lifetime because the triplet is the immediate precursor of fluorescence in the slow step of TTA

- The fluorescence is the fast kinetic step after the rate-limiting TTA has occurred

Triplet–Triplet Annihilation

- The rate constants for TTA (k_{TTA}) are generally very large and close to the rate constants of diffusion.

Substrate	**Solvent**	**T (K)**	**k_{TTA} (10^9 M^{-1} s^{-1})**
Anthracene	Toluene	258	2.74
Anthracene	Toluene	298	4.10
1,2-Benzanthracene	*n*-Hexane	296	20.3
Pyrene	Cyclohexane	Room T	7 ± 2
Pyrene	Dodecane	Room T	5 ± 1
Pyrene	Hexadecane	Room T	1.9 ± 0.2

Electron Transfer: Mechanisms and Energetics

- This section is concerned with cases where *full electron transfer* takes place either in the form of *charge transfer* between an excited and a ground state, or an *electron or hole* transfer between ground-state species of different charge

Charge transfer (electron transfer) from or to an excited state

$$^*D + A \rightarrow D^{\bullet +} + A^{\bullet -}$$

or

$$D + {}^*A \rightarrow D^{\bullet +} + A^{\bullet -}$$

Electron transfer

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

Hole transfer

$$D + A^{\bullet +} \rightarrow D^{\bullet +} + A$$

Electron Transfer: Mechanisms and Energetics

- From simple thermodynamic considerations, we expect that the rates of electron-transfer reactions will be related to the overall free energy change of reaction

- Therefore, electron-transfer reactions whose overall free energy is negative (exothermic) will be *favored*

- On the other hand, electron transfer reactions whose overall free energy is positive (endothermic) will be *disfavored*

- You may intuitively expect that the rate of electron-transfer will depend on the magnitude of exothermicity of the electron-transfer step; however, we will find out later in the Chapter that this is not exactly the case!

Electron Transfer: Mechanisms and Energetics

- We noted earlier in the Chapter that *R is *always* a better oxidizing and reducing agent compared to R
- This is true for both S_1 and T_1 states
- A simple but powerful MO basis for this generalization is shown below, where the ionization potential (IP) of the ground-state R is compared to the ionization potential (*IP) the excited state *R and the electron affinity (EA) of R is compared to the electron affinity (*EA) of *R

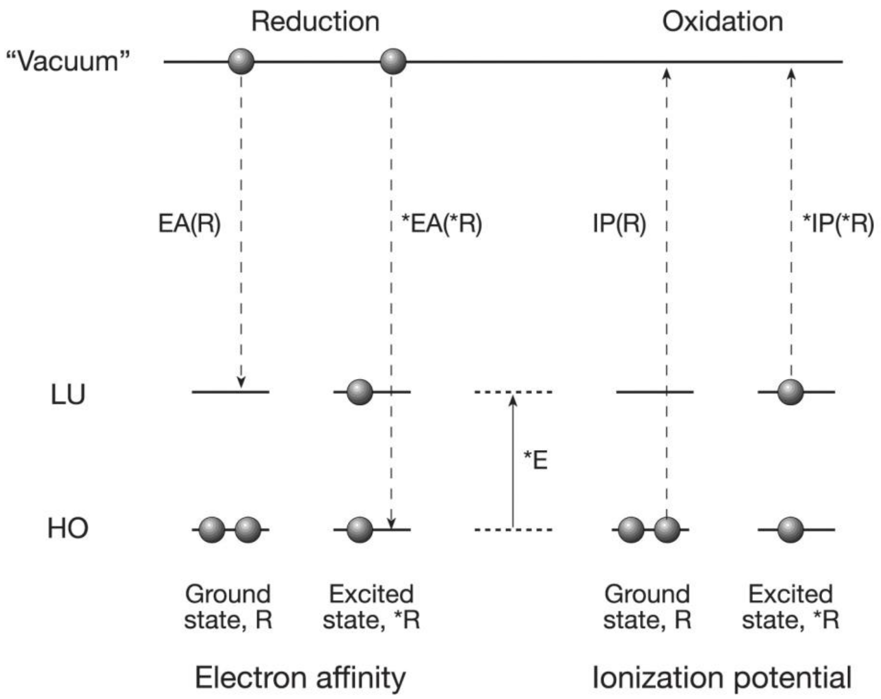


Figure 7.8 copyright 2009 University Science Books

Electron Transfer: Mechanisms and Energetics

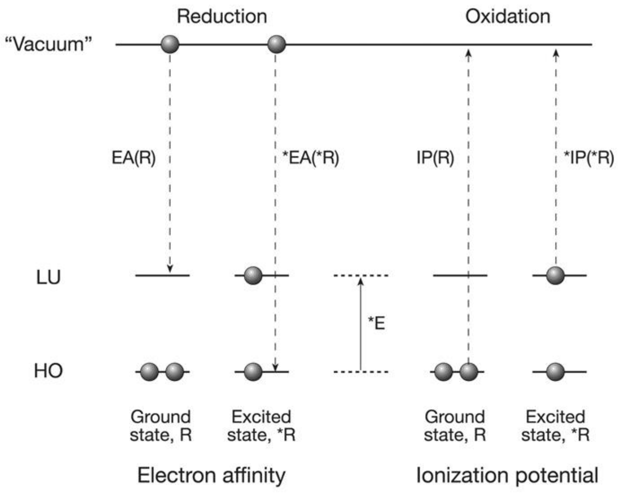


Figure 7.8 copyright 2009 University Science Books

From this figure, we can conclude that:

1. The *EA for *R is higher than the EA for R. As a result, the addition of an electron to the half-filled HO of *R is more exothermic and energy releasing than addition of an electron to the antibonding higher energy LU of R
2. The *IP is lower for *R because it takes less energy to remove the antibonding electron from the LU of *R than to remove a non-bonding or bonding electron from the HO of R

*This analysis leads to the important generalization that any *R is both a better reducing agent (lower IP) and a better oxidizing agent (higher EA) than R*

Electron Transfer: Mechanisms and Energetics

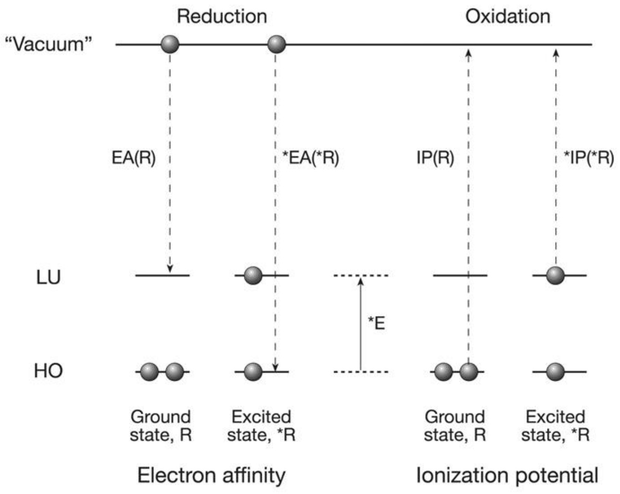


Figure 7.8 copyright 2009 University Science Books

- The energies associated with this figure refer to the situation in the gas phase (vacuum refers to the energy of the free electron not bound to a molecule)
- For the ground-state electron transfer reaction in the gas phase, the free energy for ground-state electron-transfer (ΔG_{et}) is given by eq 9:

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

$$\Delta G_{et} = (IP)_D - (EA)_A \qquad (9)$$

Electron Transfer: Mechanisms and Energetics

- For an excited donor (*D), the value of the free energy change for excited state electron transfer ($^*\Delta G_{et}$) differs from eq 9 by the magnitude of the electronic excitation energy (E_{*D})

- E_{*D} is available as free energy to do work on the electrons of *D and assist in moving an electron from the LU of *D to the LU of A in an electron-transfer process

$$^*D + A \rightarrow D^{\bullet+} + A^{\bullet-}$$

$$^*\Delta G_{et} = (IP)_D - (EA)_A - E_{*D} \tag{10}$$

$$D + {}^*A \rightarrow D^{\bullet+} + A^{\bullet-}$$

$$^*\Delta G_{et} = (IP)_D - (EA)_A - E_{*A} \tag{11}$$

Electron Transfer: Mechanisms and Energetics

- As a convention in thermodynamics, the more negative energy a free energy change has, the more exothermic is a reaction

- By comparing eq 9 with eq 10 and 11, electron-transfer in the excited state will be more favored than in the ground state, whether *R acts as a donor (eq 10) or acceptor (eq 11)

- Since addition of an electron to a molecule is generally energy releasing, the larger the value of EA, the more negative the ΔG_{et}

- Furthermore, the larger the values of $E_{*\mathrm{A}}$ and $E_{*\mathrm{D}}$, the greater the negative overall ΔG_{et} in the gas phase

Electron Transfer: Mechanisms and Energetics

- In order to deal with electron transfer in solution *quantitatively*, we to translate the gas phase values of ΔG_{et} into values of ΔG_{et} for solutions

- We would expect the solvation of the charged species produced by electron transfer to produce a significant modification of the gas phase values of ΔG

- To estimate ΔG_{et} in solution, the experimental electrochemical potentials for the oxidations $E^{0}_{(D^{+}/D)}$ and reductions $E^{0}_{(A/A^{-})}$ in solution are measured and then employed to calculate ΔG directly for solution electron transfer

- These key electrochemical parameters are commonly available or can be determined using standard electrochemical techniques (e.g., cyclic voltammetry)

Electron Transfer: Mechanisms and Energetics

In solution:

$$\Delta G_{et} \sim E^0_{(D^+/D)} - E^0_{(A/A^-)} - E_{(\,^*D\ or\ ^*A)} \qquad (12)$$

- In the literature, these calculations are often done in eV
  - 1 kcal mol^{-1} = 0.0434 eV

- It is essential to note that by convention in electrochemistry, both $E^0_{(D^+/D)}$ and $E^0_{(A/A^-)}$ are expressed as reductions; that is, both reactions are expressed as ($A + e^- \rightarrow A$) and ($D^{\bullet +} + e^- \rightarrow D$)

- Because of this convention, one must pay careful attention to the signs of the values of $E^0_{(D^+/D)}$ and $E^0_{(A/A^-)}$ when calculating ΔG

- The “~” in eq 12 is there to emphasize that this is only an approximate expression

Electron Transfer: Mechanisms and Energetics

- There are two approximations that are commonly required for quantitative analysis of photochemical reactions involving electron transfer:

1) The $E_{(\,^*D\ or\ ^*A)}$ term normally represents PE, and therefore is always an enthalpy (ΔH), not a free energy (ΔG). The ΔG includes an entropy term (ΔS). The ΔS term is often neglected or assumed to be negligible

2) There is a Coulombic energy gain associated with bringing two particles of opposite charge ($D^{\bullet+}$ and $A^{\bullet-}$) close together. The Coulombic contribution to ΔG decreases as the separation between the charged species increases or as the dielectric constant of the solvent increases. While significant for non-polar solvents, this becomes negligible for polar solvents

Electron Transfer: Mechanisms and Energetics

- Now let’s consider the effect of the Coulombic stabilization experiences by two oppositely charged ions

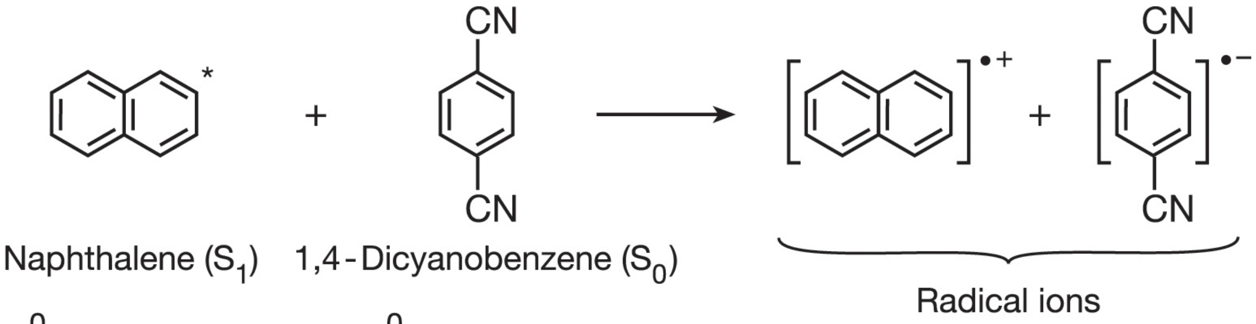
- By introducing the “Coulombic term” for stabilization of opposite charges, eq 12 becomes:

$$\Delta G_{et} \approx E^0_{(D^+/D)} - E^0_{(A/A^-)} - E_{(\,^*D \; or \; ^*A)} + \Delta E_{Coulombic} \tag{13}$$

- In polar solvents, like water and acetonitrile, the Coulombic term is negligible (very small compared to the value of $E_{(\,^*D \; or \; ^*A)}$) and can often be ignored from the calculation

Electron Transfer: Mechanisms and Energetics

- Let's calculate ΔG_{et} for the electron transfer reaction below:



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

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

$$\Delta G_{et} = E^\circ_{(D^+/D)} - E^0_{(A/A^-)} - E_{*D} + \Delta E_{\cancel{coulombic}}$$

Solvent is MeCN so this term can be dropped

$$\Delta G_{et} = 1.60 - (-1.64) - 3.94$$

$$\boxed{\Delta G_{et} = -0.7 \text{ eV} = -16 \text{ kcal mol}^{-1}}$$

Stern–Volmer Analysis

- Quenching of fluorescence often occurs as the result of an electron-transfer reaction

- A kinetic analysis of bimolecular electron-transfer quenching of fluorescence between appropriate *R and M pairs, termed a "Stern–Volmer analysis", provides an experimental method for the measurement of the rate constant (k_{et})

- The Stern–Volmer equation is as follows:

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \qquad (14)$$

where I_0 and I are the fluorescence intensities in the absence and presence of quencher, respectively, [Q] is the concentration of quencher and K_{SV} is the Stern–Volmer quenching constant

Stern–Volmer Analysis

- The Stern–Volmer quenching constant (K_{SV}) is given by:

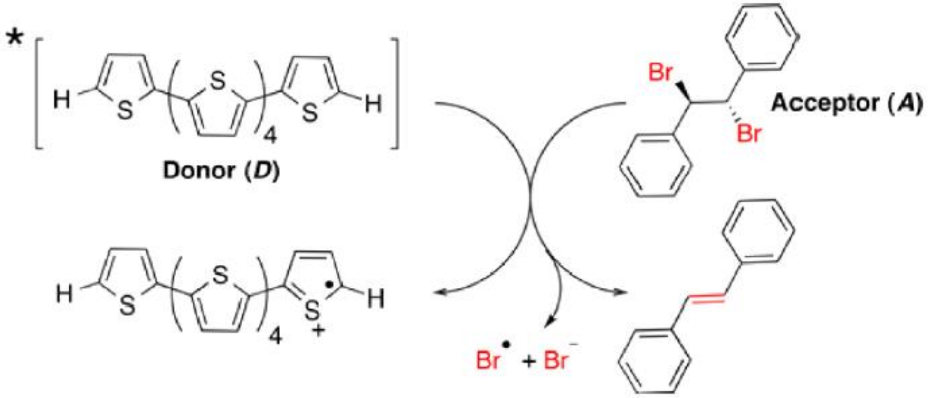
$$K_{SV} = k_q \tau_0 \tag{15}$$

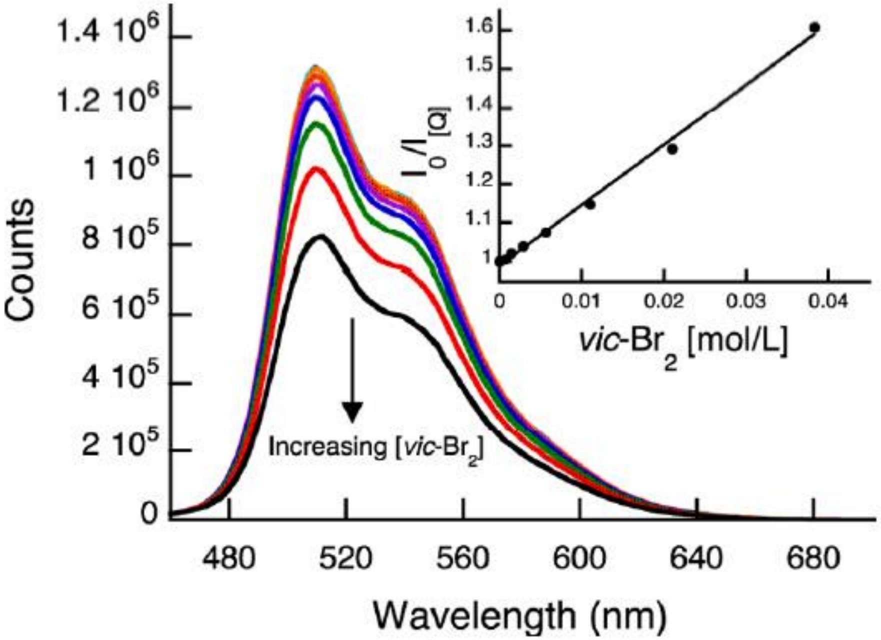
where k_q is the biomolecular quenching constant ($k_q = k_{et}$ for quenching by electron-transfer) and τ_0 is the excited state lifetime in the absence of quencher

- Quenching data are usually presented as plots of I_0/I vs. [Q] because I_0/I is expected to be linearly dependent on [Q]
- A plot of I_0/I vs. [Q] yields an intercept of 1 on the y-axis and a slope equal to K_{SV}
- One useful parameter is that the K_{SV}^{-1} is [Q] at which $I_0/I = 2$ or 50% emission intensity is quenched

Stern–Volmer Analysis

- An example of Stern–Volmer analysis in action:





K_{SV} = 15.6 M^{-1}
k_q = 1.93 x 10^{10} M^{-1} s^{-1}

McTiernan, C. D.; Pitre, S. P.; Scaiano, J. C. *ACS Catal*. **2014**, *4*, 4034.

Electron Transfer: Mechanisms and Energetics

- By using Stern–Volmer analysis, values of k_{et} have been determined for a number of systems as a function of free energy for the electron-transfer process

- For example, the dependence on k_{et} for electron-transfer fluorescence quenching in acetonitrile by a variety of quenchers on the exothermicity for the electron-transfer reactions is shown below:

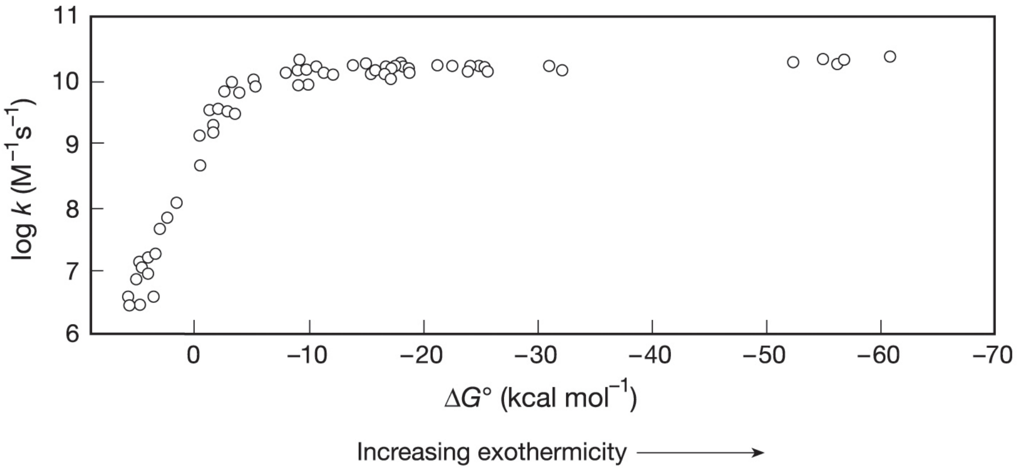


Figure 7.10 copyright 2009 University Science Books

- Such plots of k_{et} vs. $\Delta G°$ are known as “Rehm–Weller plots”

Electron Transfer: Mechanisms and Energetics

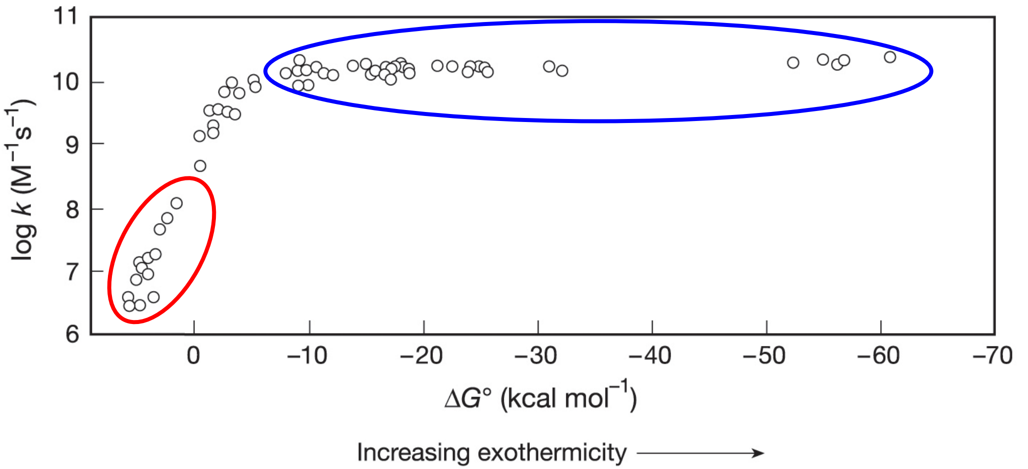


Figure 7.10 copyright 2009 University Science Books

- The measured values of k_{et} span the range of ~ 10^6 to ~ 2 x 10^{10} M^{-1} s^{-1}, with the latter being close to k_{diff} in MeCN
- The free enthalpy change for the electron-transfer processes investigated varied from ~ 5 to −60 kcal mol^{-1}
- The plot of k_{et} vs. $\Delta G°$ shows a steep decrease in rate constants for more positive $\Delta G°$ values for endothermic reactions ($\Delta G° > 0$)
- The most striking feature is that the value of k_{et} reaches a plateau value of ~ 2 x 10^{10} M^{-1} s^{-1} after an exothermicity of ~ 10 kcal mol^{-1} and that value k_{et} remains the diffusion-controlled value to the highest negative values of $\Delta G°$ achievable

Electron Transfer: Mechanisms and Energetics

- It can be concluded that when the value of $\Delta G°$ approaches about −10 kcal mol^{-1}, the process being measured is controlled by something other than electron transfer

- Indeed, the value of k_{et} in the plateau region approximately corresponds to the expected rate constant for diffusional processes (k_{diff}) in acetonitrile (~ 2 x 10^{10} M^{-1} s^{-1})

- It can be concluded that k_{et} ceases to be rate-limiting in the plateau region, and diffusion becomes the rate-limiting process

- *This finding means that the true rate constant of electron transfer cannot be measured in the plateau region, because diffusion is the rate-limiting step, not electron transfer*

Theory of Electron Transfer

- An electron transfer reaction involves the creation of a pair of ions ($D^{\bullet+}$ and $A^{\bullet-}$), which will interact strongly with the solvent

- The solvent, which is not considered explicitly for electron transfer processes, may have to undergo considerable structural “reorganization” to accommodate and stabilize the new charged molecular system, $D^{\bullet+} + A^{\bullet-}$

- Therefore, the solvent reorganization and the influence of opposite charges on themselves and the solvent (Coulombic term) must be considered in the quantitative aspects of electron transfer

Libby Theory of Electron Transfer

- The beginnings of the modern theory of electron transfer may be traced back to a seminal paper published by W. F. Libby (*J. Phys. Chem*. **1952**, *56*, 863), where Libby correctly pointed out the potential importance of "solvent reorganization" in controlling the rates of electron-transfer reactions, that is, $D + A \rightarrow D^{\bullet +}$ and $A^{\bullet -}$
- Consider an electron-transfer reaction in a very polar solvent, like water or acetonitrile
- When a neutral electron-donor molecule D (solvated) converts to an ion $D^{\bullet +}$ (solvated), the electronic structures D and $D^{\bullet +}$ are considerably different with respect to their charge distribution
- It is therefore expected that the solvation spheres around D (solvated) and $D^{\bullet +}$ (solvated) must undergo considerable reorganization of the solvent dipoles around the nascent electrical charges generated about $D^{\bullet +}$ and $A^{\bullet -}$, as the electron is being transferred
- The change in free energy resulting from reorganization of the solvent molecules, as reactants proceed to products during an electron transfer reaction, is termed "solvent reorganization energy"

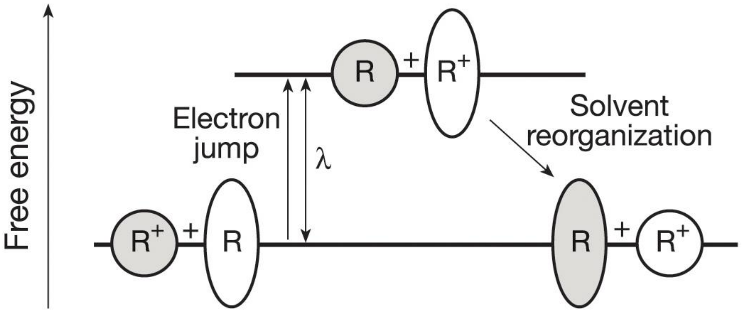
Willard F. Libby
American Physical Chemist
Nobel Prize winner in 1960

Libby Theory of Electron Transfer

- Let’s consider the simple charge translocation reaction below:

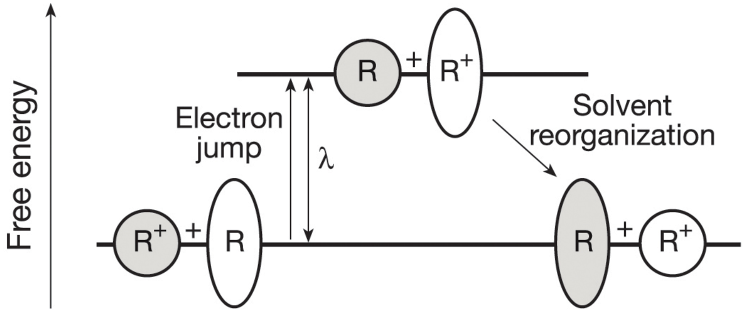
$$R^{\bullet +}(\text{solvated}) + R(\text{solvated}) \rightarrow R(\text{solvated}) + R^{\bullet +}(\text{solvated})$$

- In his theory, Libby argued that electron transfer would be a much faster process than intramolecular bond reorganization or solvent organization, so the solvent structural changes would *follow* the transfer or “jump” of the electron from R to $R^{\bullet +}$



- The figure above schematically shows his concept of the solvent change that must occur about R and $R^{\bullet +}$ during the electron transfer process, assuming the electron jump occurs first, followed by reorganization of the internal structure of the reactants and external structure of the solvent

Libby Theory of Electron Transfer

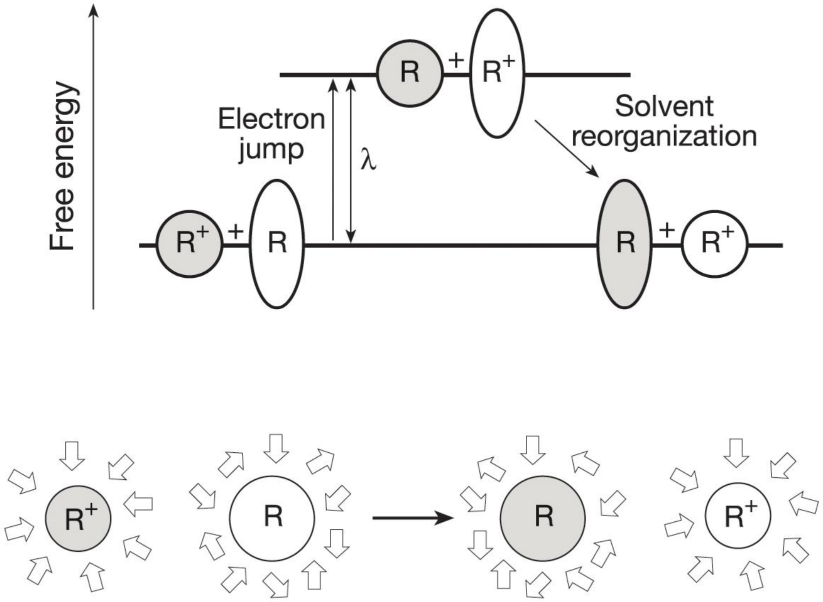


- The electron jump from R to $R^{\bullet +}$ is analogous to the electron jump from a HO to LU that leads to the formation of an electronically excited state

- From this analogy, the electron jump is expected to occur “vertically” and follow the Franck–Condon principle, which states that the geometry of the products formed by an electron jump (an electron transfer) is the same as the geometry of the reactants

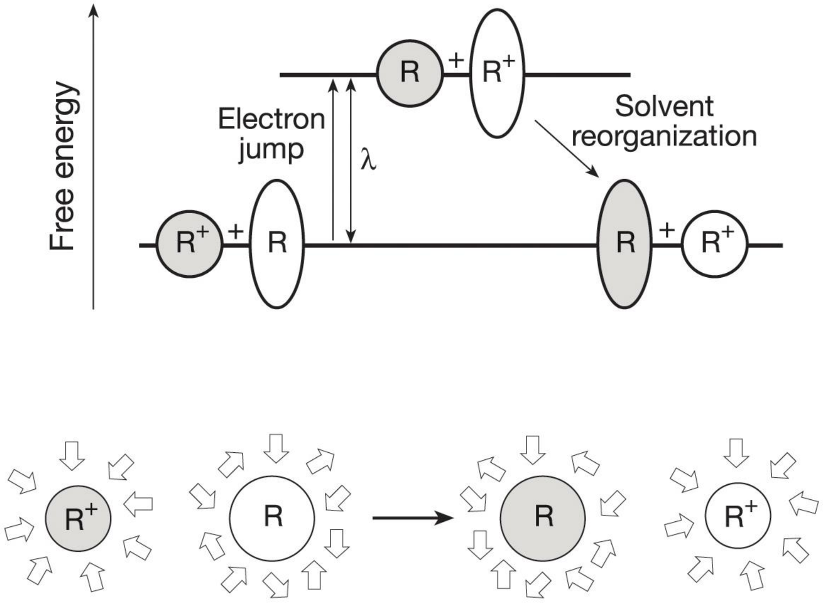
- In the figure above, this feature is illustrated by showing $R^{\bullet +}$ as having a smaller spherical shape (the positive charge will pull the electrons in closer to the nuclear framework) than R, which is more diffuse and is schematically given an oval shape

Libby Theory of Electron Transfer



- After electron transfer occurs, the immediate shapes of R and $R^{\bullet+}$ are “structurally out of order”, since immediately after an electron jump, $R^{\bullet+}$ still has a small spherical shape that it had just before the electron transfer, and the newly formed R still has the larger oval shape it had just before the electron transfer
- Furthermore, immediately after the electron-transfer event, the solvent molecules are still oriented about the newly formed $R^{\bullet+}$ as if it were R and about the newly formed R as if it were $R^{\bullet+}$
- This situation is clearly kinetically unstable with respect to the potential and free energy of the system

Libby Theory of Electron Transfer

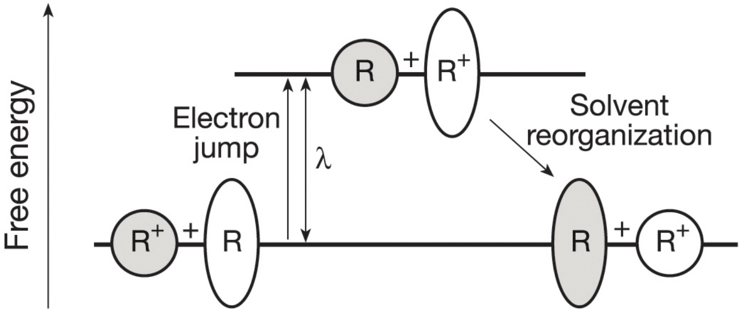


- Two types of reorganization will have to occur

1) An electronic and vibrational reorganization associated with the electron transfer, termed *internal molecular reorganization*

2) A solvent reorganization associated with the solvent reorientation to accommodate the new electronic structures produced by electron transfer, termed *external solvent reorganization*

Libby Theory of Electron Transfer



- From the representation of electron transfer above, the “vertical” jump is analogous to the absorption of a photon and would require a significant amount of positive energy input if it occurs before the internal and external structural reorganizations have time to occur (symbol λ)

- *This positive energy (λ) corresponds to the total internal and external reorganization energy that is required in an isoenergetic electron transfer reaction*, such as:

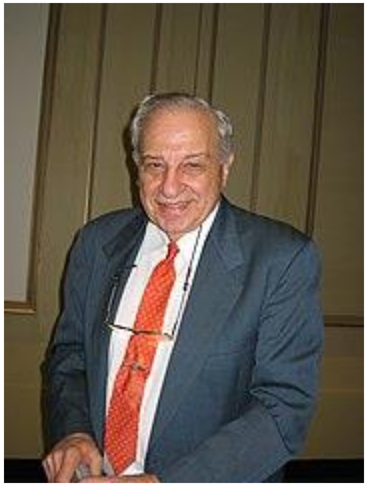
$$R^{\bullet+}(\text{solvated}) + R(\text{solvated}) \rightarrow R(\text{solvated}) + R^{\bullet+}(\text{solvated})$$

Marcus Theory of Electron Transfer

- Marcus pointed out that for thermal reactions a vertical jump from the ground state to the excited state requires the very unlikely sudden input from a considerable amount of *thermal energy*

- Such a process would be plausible only if the system absorbed a photon whose energy = $\lambda = h\nu$

- Therefore, Marcus concluded that a vertical jump could not plausibly be rate-limiting in a ***thermal*** electron-transfer reaction but would be plausible for a photoinduced electron-transfer reaction



Rudolph Marcus
Canadian Chemist

Marcus Theory of Electron Transfer

- Marcus proposed that the rate-limiting feature of an elementary *thermal* electron-transfer process requires only that the molecules and solvent involved in the electron transfer overcome an energy barrier at the crossing point between two PE surfaces (see next slide)

- Moving along the reaction coordinate to the crossing point corresponds to the reorganization of the reactants and solvent to achieve the lowest energy path for electron transfer

- Once the reorganization of the molecular and solvent structures have taken place and the representative point is at the crossing point for the intersection of the PE surface for the reactants and products (the transition state), a weak electronic interaction can trigger the electron-transfer event from R to $R^{\bullet +}$

Marcus Theory of Electron Transfer

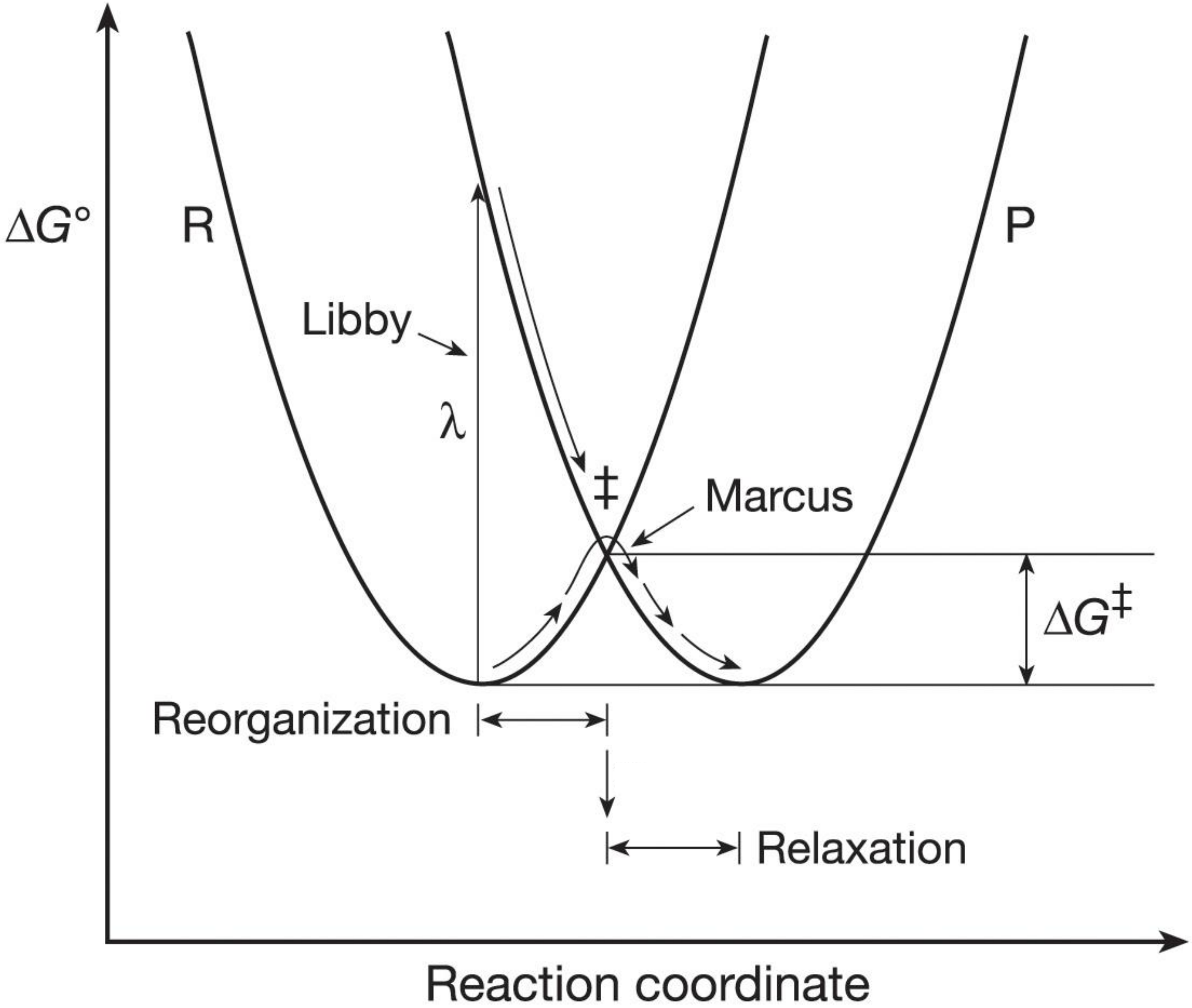


Figure 7.12 copyright 2009 University Science Books

Marcus Theory of Electron Transfer

- From the figure on the previous slide, we can define several important parameters that will be the basis for the quantitative computation of k_{et} from Marcus theory:

1) The *reorganization energy*, λ corresponds to the vertical transition from the minimum of the ground-state parabola of the reactants (R) to the intersection with the parabola for the products (P). This thermal vertical transition is equivalent to the absorption of a photon ($h\nu = \lambda$), which causes a FC electron transfer. Recall from Libby theory that λ can be viewed as the organization energy required for an electron transfer before any *inner-* (molecular) or *outer-sphere* (supramolecular) organization

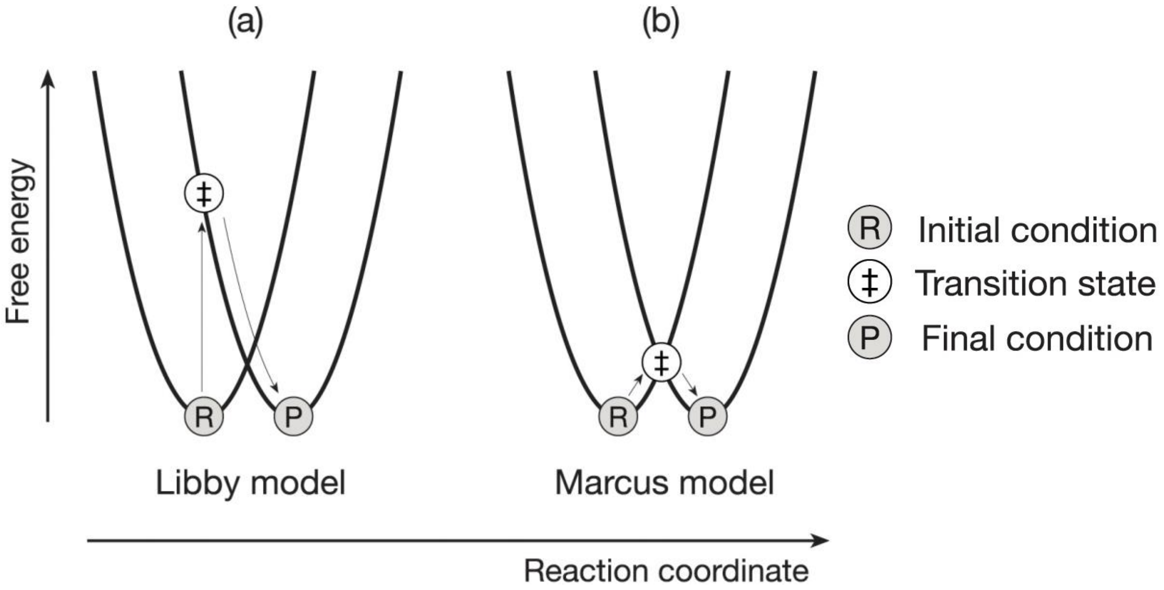
Marcus Theory of Electron Transfer

2) The *free energy of activation* ($\Delta G^{‡}$) represents the free energy required to reach the transition state configuration (TS‡) starting from the minimum of the reactant PE curve. The reactants need to *reorganize* their nuclei and electrons both internally and externally to meet the requirements for electron transfer to be possible. The term “reaction coordinate” here considers not only the nuclear coordinates of R (inner sphere) but also the coordinates of the environment, specifically the solvent rearrangement (outer sphere). Once the TS‡ has been reached, it can proceed to the product surface, or “reflected” back to the reactants

3) The *thermodynamic free energy of reaction* ($\Delta G°$) represents the difference in free energy between reactants and products (minima of the parabolas representing R and P)

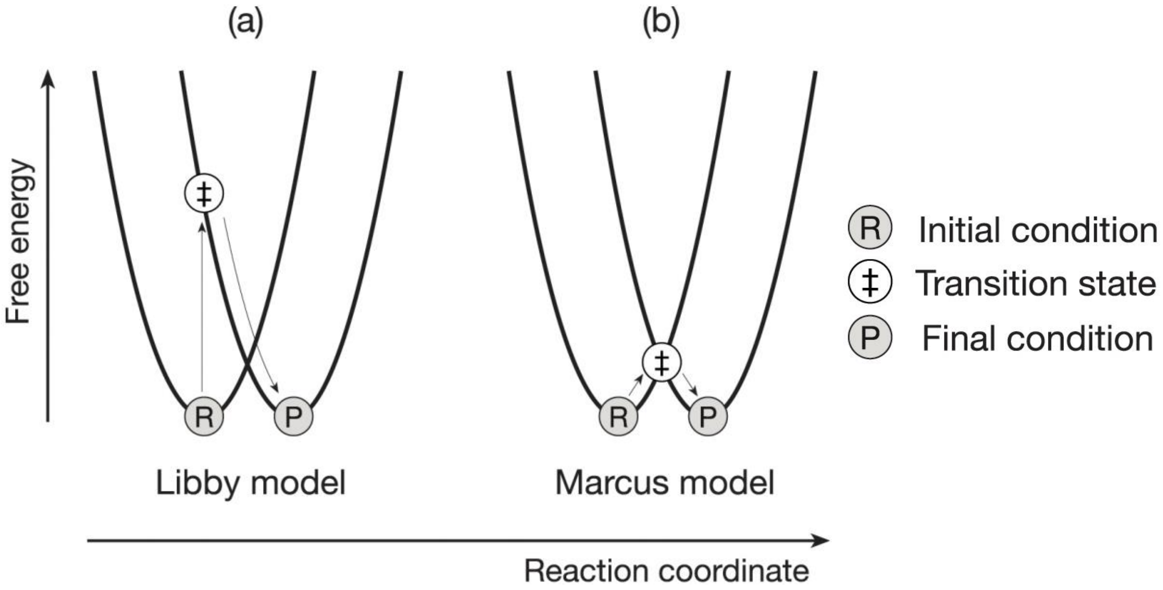
- Now, we shall see how Marcus’ insight was to use information from the geometry of intersecting PE curves, described mathematically as parabolas, to qualitatively relate k_{et} to λ, $\Delta G°$ and $\Delta G^{‡}$

Marcus Theory of Electron Transfer



- The essential difference between the early Libby and current Marcus theories of electron transfer is highlighted above
- In Libby theory, the representative point is assumed to pay an initial steep energetic price by jumping from the reactant to the product curve, vertically at first and then passing onto product (a)
- There is no obvious source of thermal energy (equal to λ) required for the electron to jump, and therefore it is implausible

Marcus Theory of Electron Transfer



- In Marcus theory, the representative point pays a much lower price to achieve the transition state ‡ for electron transfer
- Thermal energy is used for reorganizing the molecular structure (inner sphere) and the solvent structure (outer sphere) along the reaction coordinate and for overcoming the energy barrier at the crossing point ($TS^{‡}$) of the two energy curves (b)
- At surface crossing, the free energy of the system is the same whether the electron is transferred to the reactant or to the product

Marcus Theory of Electron Transfer

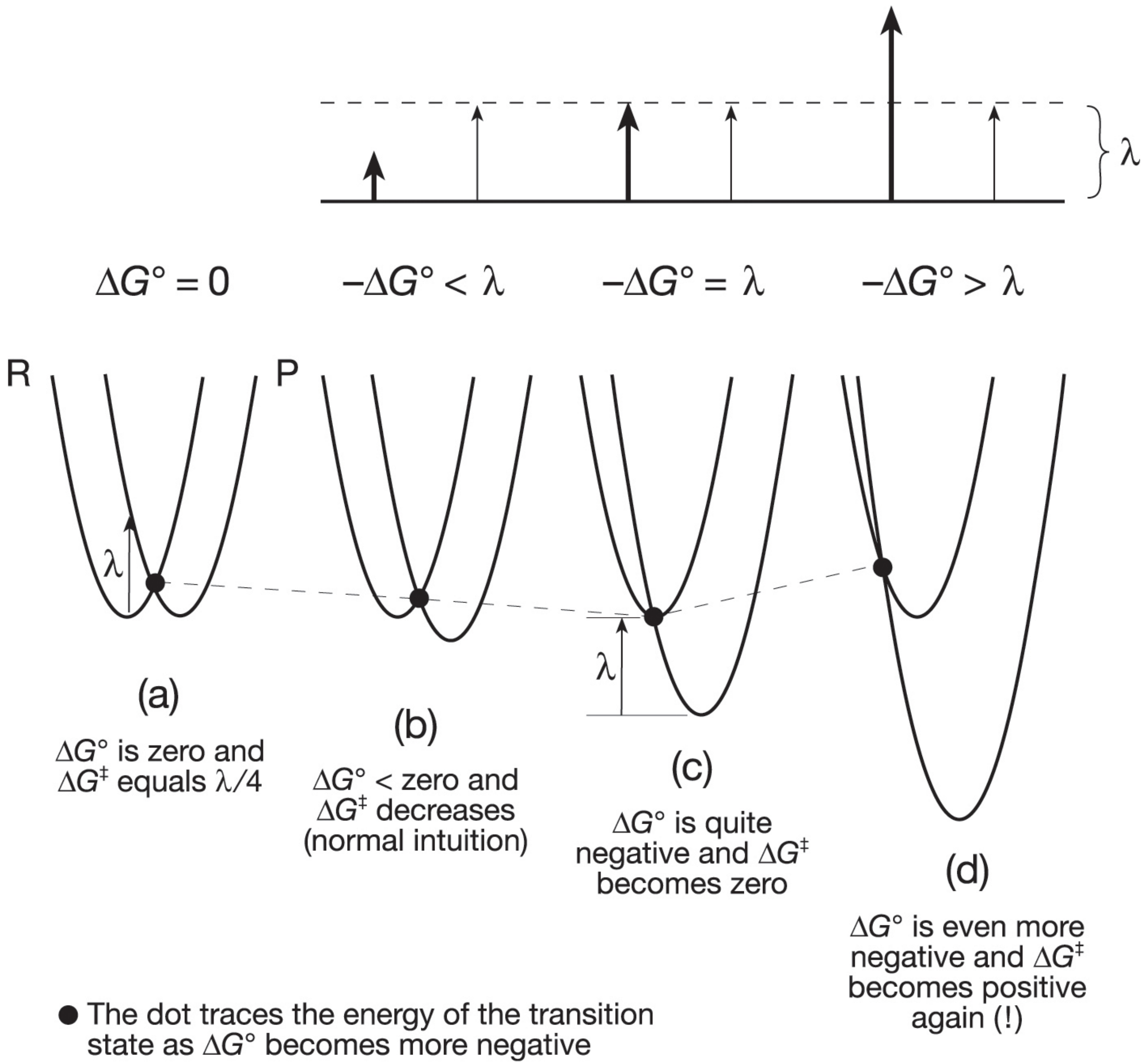
- Chemists are accustomed to the principle that, for a series of structurally related reactions, as the reaction becomes more exothermic ($\Delta G°$ becomes more negative), the activation energy ($\Delta G^{‡}$) becomes smaller

- The basis for this principle can be understood by considering the behavior of the crossing point (which corresponds to $\Delta G^{‡}$) of the two parabolas as the minimum of the parabola corresponding to the products is decreased (along y-axis) relative to the minimum for the curve corresponding to the reactants, without displacing the two curves along the reaction coordinate (x-axis)

- As a reaction becomes increasingly exothermic, the values of $\Delta G^{‡}$ change and reflect the vertical displacement of the reactant (R) and product (P) energy curves

- The next slide shows the evolution of the PE curves as $\Delta G°$ becomes more negative

Marcus Theory of Electron Transfer



$\Delta G^\circ = 0$ $-\Delta G^\circ < \lambda$ $-\Delta G^\circ = \lambda$ $-\Delta G^\circ > \lambda$

(a)

ΔG° is zero and
$\Delta G^\ddagger$ equals $\lambda/4$

(b)

ΔG° < zero and
$\Delta G^\ddagger$ decreases
(normal intuition)

(c)

ΔG° is quite
negative and $\Delta G^\ddagger$
becomes zero

(d)

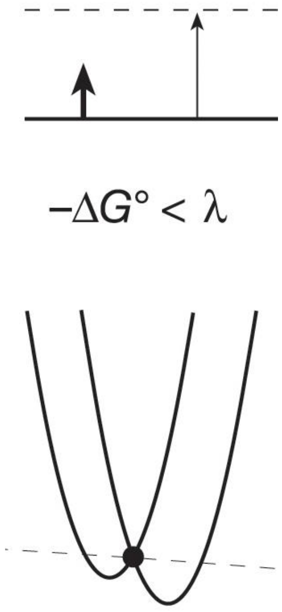
ΔG° is even more
negative and $\Delta G^\ddagger$
becomes positive
again (!)

● The dot traces the energy of the transition state as ΔG° becomes more negative

Figure 7.14 copyright 2009 University Science Books

Marcus Theory of Electron Transfer

- Let’s start by examining case (b)
- In this case, the energy barrier $\Delta G^{\ddagger}$ clearly decreases as $\Delta G°$ becomes more negative
- The decrease in $\Delta G^{\ddagger}$ is simply a consequence of geometry, since keeping the shape of the curves fixed on the x-axis simply moves the left-hand portion of the product curve down in energy relative to the minimum of the reactant curve
- As a result, the crossing point (TS‡) corresponding to $\Delta G^{\ddagger}$ moves closer and closer to the minimum of the reactants PE curve and the magnitude of $\Delta G^{\ddagger}$ decreases

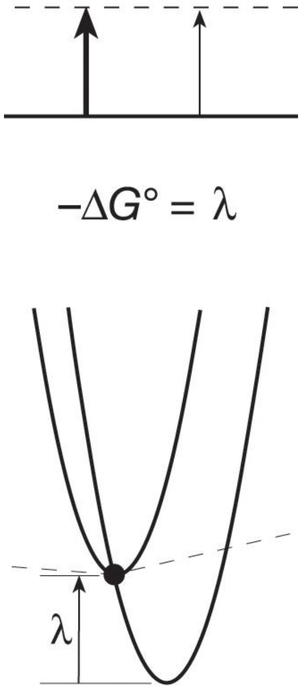


(b)

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

Marcus Theory of Electron Transfer

- When a certain energy value is reached, case (c), the crossing point passes through the minimum of the reactant’s curve
- For this value of $\Delta G°$, *there is no barrier to electron transfer and the rate of electron transfer (*k_{et}*) will be at a maximum*
- Marcus showed that the value of $\Delta G°$, for which $\Delta G^{\ddagger} = 0$, is equal to the negative value of λ
- Thus, when $\Delta G° = -\lambda$, the value of $\Delta G^{\ddagger} = 0$, and there is no activation energy required for electron transfer!



(c)

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

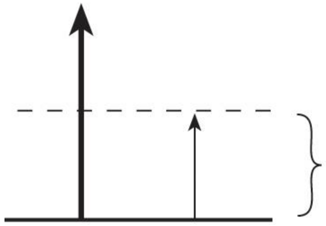
Marcus Theory of Electron Transfer

- What happens when $\Delta G° > -\lambda$? {case (d)}

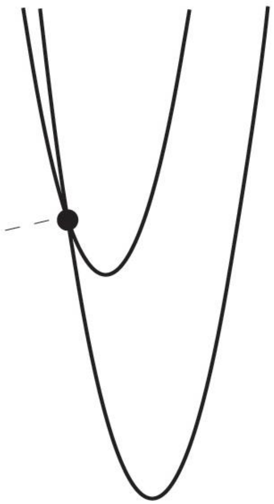
- The energy curve of the product now intersects *above the minimum of the reactant curve on the left as the value of* $\Delta G°$ *becomes greater than the value of* $-\lambda$

- As the reaction becomes more exothermic, the point of intersection moves to higher and higher energies

- Since the point of intersection of the energy curves corresponds to the activation energy, $\Delta G^{\ddagger}$, which determines the reaction rate, we are forced to nonintuitively conclude that *the rate of electron transfer will slow down as the reaction becomes more exothermic beyond the point of* $\Delta G° = -\lambda$*!*



$-\Delta G° > \lambda$



(d)

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

Marcus Theory of Electron Transfer

- The slowing down of the electron-transfer rate with increasing negative value of $\Delta G°$ beyond the point that $\Delta G° = -\lambda$ is the basis for the so-called "*inverted*" region of electron-transfer

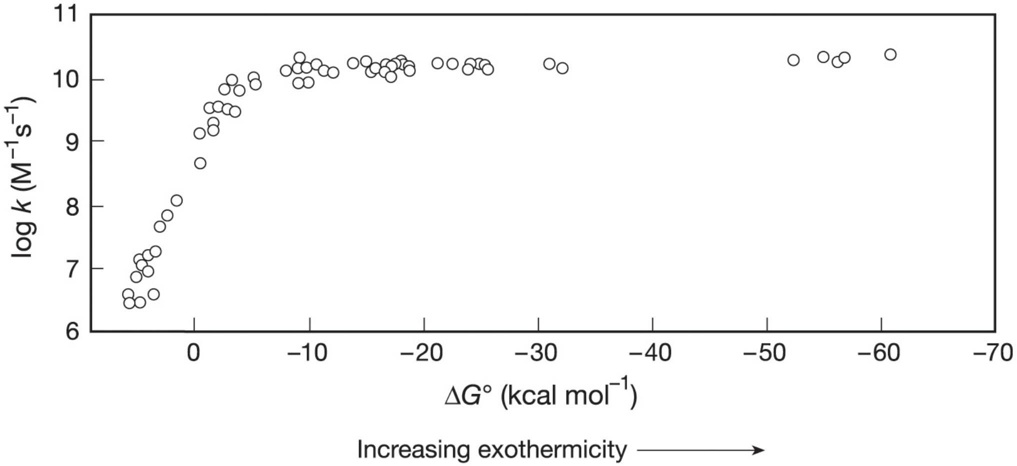
- The *inverted region* is the region of free energies for which the rate of electron transfer decreases with increasing negative value of $\Delta G°$

- The region for which the rate of electron transfer increases with increasing negative value of $\Delta G°$ is termed the "*normal*" region of electron transfer

- The region at or near $\Delta G° = -\lambda$ is termed the "*barrierless*" region, since in this region $\Delta G^{\ddagger} \sim 0$

Experimental Verification of the Marcus Inverted Region

- Marcus’ prediction of the existence of a counterintuitive “inverted” region for electron transfer involving electronically excited states (*R) where an increased driving force ($\Delta G°$) leads to decreased reactivity posed a major challenge to experimentalists
- Photoinduced electron transfer are obvious candidates to test the existence of the inverted region since the electronic excitation energy contributes to the overall reaction exothermicity, thereby enhancing the possibility of a system having a very negative value of $\Delta G°$ and being in the inverted region
- However, before the 1980s, experimental examples of photoinduced electron transfer showed that k_{et} did not decrease as the exothermicity became very large, but instead reached the limiting value of diffusion



Experimental Verification of the Marcus Inverted Region

- The absence of experimental evidence for photoinduced electron transfer in an inverted region meant either:
  - The inverted region for electron transfer could not be reached
  - The inverted region did not exist
  - The inverted region was masked by diffusion
- The latter would be the case if once $k_{et} = k_{diff}$, k_{et} was no longer rate-limiting

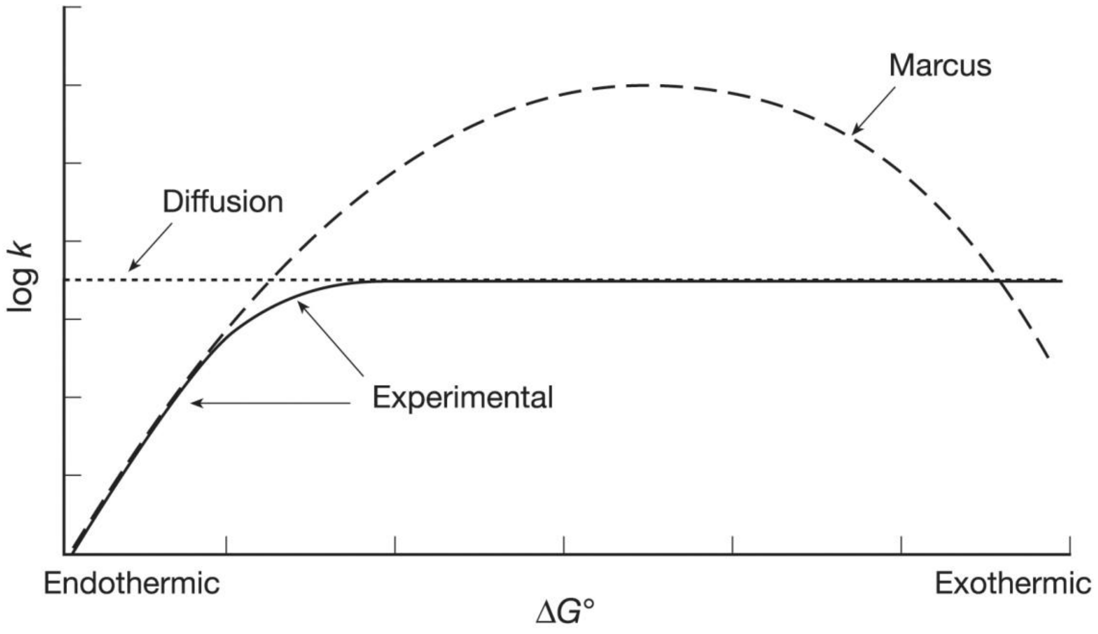


Figure 7.16 copyright 2009 University Science Books

Experimental Verification of the Marcus Inverted Region

- In the previous diagram, k_{et} is assumed to be in the “normal region” and to increase at first with increasing exothermicity up to a certain value of $\Delta G°$

- After this value of $\Delta G°$ is reached, k_{et} is assumed to be faster than k_{diff} for further increases in $\Delta G°$

- Therefore, from this point on, the rate of quenching is limited by the rate of diffusion, not the rate of electron transfer

- The experimental value is expected to blend the two regions, rather than simply reflect the minimum of the two possible rate constants

Experimental Verification of the Marcus Inverted Region

- Finding experimental examples of the inverted region required a strategy that avoided the diffusion control limiting electron-transfer reaction

- Three strategies have proven successful for the experimental observation of the inverted region:

1) The elimination of diffusion between D and A by running the electron transfer in a rigid medium where diffusion is strongly inhibited
2) The elimination of diffusion for D and A by attaching D and A to a rigid molecular framework that serves as a spacer, D(Sp)A, that allows for electron transfer in liquids but prevents diffusion of D and A
3) Allowing diffusion of D and A and electron transfer to form $D^{\bullet+}$ and $A^{\bullet-}$ to occur but measuring the unimolecular rate of back electron transfer from $D^{\bullet+}$ to $A^{\bullet-}$ to form D and A

Experimental Verification of the Marcus Inverted Region

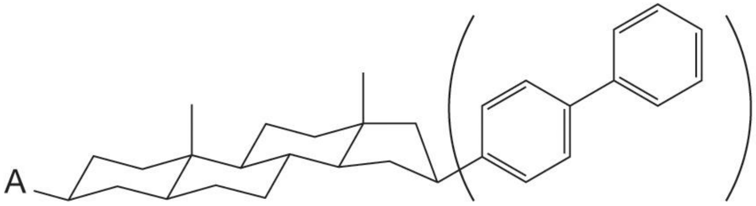
- The first successful approach that provided convincing evidence of the inverted region was developed by Closs and Miller

- They investigated a D(Sp)A system in a rigid medium (combining strategies 1 and 2 from the previous slide)

- The reaction studied was an electron transfer involving charge translocation following capture of an electron generated by pulse radiolysis by the D moiety of the D(Sp)A system

$$\mathrm{D(Sp)A} + \mathrm{e}^{\bullet -} \rightarrow \mathrm{D}^{\bullet -}\mathrm{(Sp)A}$$

$$\mathrm{D}^{\bullet -}\mathrm{(Sp)A} \xrightarrow{k_{et}} \mathrm{D(Sp)A}^{\bullet -}$$



D(Sp)A

Unnumbered figure 7.1 copyright 2009 University Science Books

Experimental Verification of the Marcus Inverted Region

- The figure below shows their experimental results for eight different acceptors compared to the calculated theoretical curve
- The theoretical value of λ is ~ 1.2 eV or ~ 27.7 kcal mol^{-1}
- As predicted, when $-\Delta G° > \lambda$, k_{et} decreases with increased exothermicity

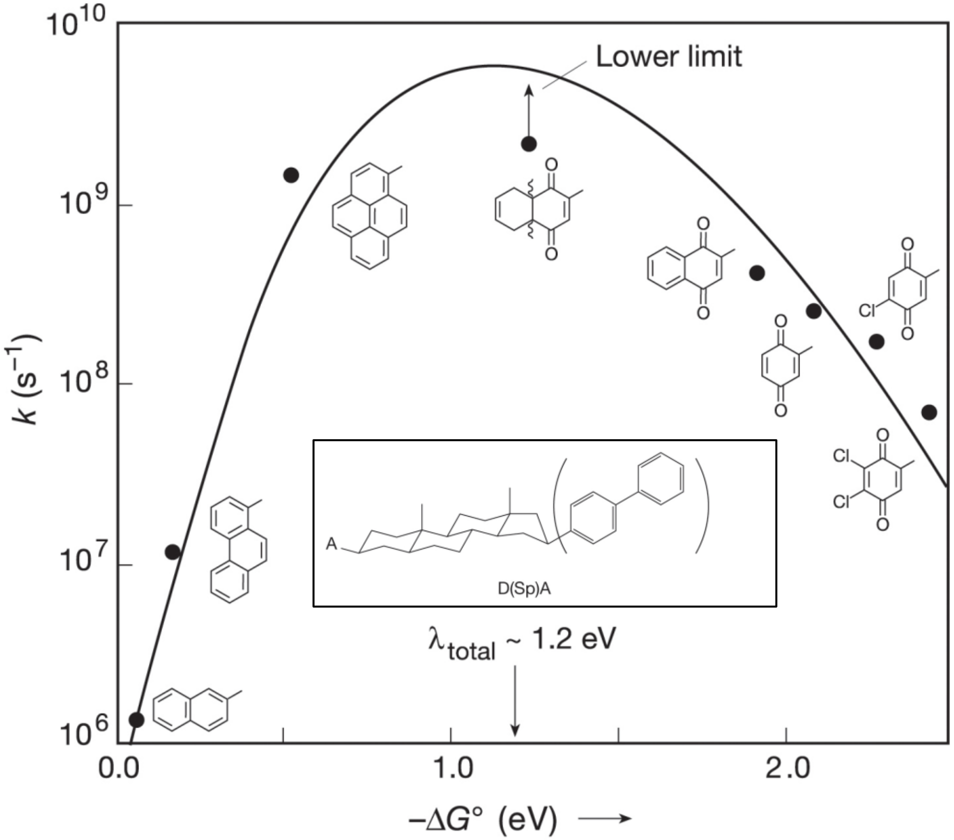


Figure 7.17 copyright 2009 University Science Books

Up Next…

The Photochemistry of $Ru(bpy)_3Cl_2$