Chapter 7

Energy and Electron Transfer

We have seen in Chapter 6 that initial frontier orbital overlap results in weak electronic exchange interactions between an electronically excited state, \( ^*R \), and a second molecular species, M (or between \( ^*R \) and groups which are accessible intramolecularly). These interactions often determine the reaction coordinate (lowest energy surface pathway) followed by the representative point, \( r \). Both electron transfer and electronically energy transfer between \( ^*R \) and M can be triggered by initial orbital overlap and electron exchange interactions. In this chapter we shall consider the paradigms for electronic energy transfer and for electron transfer processes together since both processes possess a common orbital description. Frontier molecular orbital theory, predicts that at the beginning of the orbital interactions both electron charge transfer and electron energy transfer processes will be very similar electronically. Whether electron charge transfer or energy transfer will occur will depend on a number of factors that shall be described in this Chapter. (Although electron transfer requires orbital overlap in all cases, we shall describe later in the Chapter a second important mechanism of energy transfer that does not require orbital overlap, but can occur through space through dipole-dipole interactions.)

To set up the discussion, let us consider Scheme 7.1, which shows the paradigm of energy transfer and electron transfer in terms of three possible results of the orbital interactions of \( ^*R \) and M. The first process is electronic energy transfer and the second and third processes are electron transfers. In the energy transfer process it is understood that \( ^*R \) will always be an energy donor and M will always be an energy acceptor. In the electron transfer process \( ^*R \) may be an electron donor or an electron acceptor as we have seen in Chapter 6 (Fig.
6.10). We shall use the symbol eD to indicate when *R (or M) is an electron donor and the symbol eA to indicate when *R (or M) is an electron acceptor.

The rate of the energy transfer process, *R + M → R + *M is determined mainly by the whether the overall process is energetically downhill with respect to the thermodynamics of the overall energy transfer process, i.e., the energy process usually proceeds at a rapid rate if E(*R) > E(*M), i.e., the electronic excitation energy available to *R is sufficient to electronically excite *M. The rate of the electron transfer process, *R + M → I(R+/M- or R-/M+), is determined not only by the electronic excitation energy or *R, but also by the thermodynamics of the overall electrochemical redox characteristics of the overall electron transfer process. Although energy and electron processes have qualitative similarities at the initial stages of orbital interactions, the two processes become quantitatively different in an important respect as the representative point proceeds along the reaction coordinate. The energy transfer process from *R does not usually create a large redistribution of charge, but produces a neutral electronically excited state, *M. The electron transfer process, on the other hand, creates a reactive intermediate, usually a radical ion pair I(R+/M- or R-/M+), whose energy characteristics will be very sensitive to polar effects such as the solvent solvation of the charged ions.

\[
\begin{align*}
*R + M & \rightarrow R + *M & \text{Electronic energy transfer (*R an energy donor)} \\
*R(eD) + M(eA) & \rightarrow I(R^+/M^-) & \text{Electron transfer (*R an electron donor)} \\
*R(eA) + M(eD) & \rightarrow I(R^-/M^+) & \text{Electron transfer (*R an electron acceptor)}
\end{align*}
\]

**Scheme 7.1** The mechanistic paradigm for electronic energy transfer and electron transfer.
The rates and efficiencies of energy and electron transfer processes will depend on the balance of several key processes: (1) the diffusional process that bring the reactants, *R and M, together to within a critical separation at which energy transfer or electron transfer can occur; (2) the competition of the reactants between separation or reaction after the critical separation has been achieved, and (3) the successful irreversible separation of the primary products after either energy or electron transfer has occurred.

We will deal initially with the mechanisms by which energy and electron transfer can take place, without being concerned with the mechanisms by which donors and acceptors approach within the distances required for reaction. We will later deal with the diffusional and structural processes that are responsible for bringing *R and M to within a “critical distance” for energy or electron transfer. We will also consider systems for which the reactants, *R and M are separated by a molecular “spacer” framework with is rigid and fixed during the time of the energy or electron transfer events.

For freely diffusing reagents, *R and M, the initial energy transfer and/or electron interactions to occur, require a delivery process (e.g., diffusion) that leads to an encounter which brings the reactants to critical separation distance which allows for effective orbital interactions. For concreteness, let us assume that this separation distance is that achieved by actual molecular collisions of *R and M. In this model, *R and M must become neighbors in a solvent cage, i.e., the reactants are “caged” by the walls created by the solvent. After an encounter has occurred, the probability of energy or electron transfer requires certain conditions to be met. As always, the process will require conservation of energy and momentum. Certain features in the molecules, their relative orientation and the nature and magnitude of their interaction with the environment (i.e., their enthalpic and entropic reorganization energy) all may play a role in determining whether a
given encounter leads to a successful electron or energy transfer. Let us now elaborate on these features.

### 7.1 Mechanisms for Energy and Electron Transfer

Energy transfer and electron transfer reactions induced by electron exchange interactions are covered jointly in this Chapter to emphasize how closely interrelated the two processes are conceptually and mechanistically in terms of orbital interactions. Figures 1a and 1b show the basic orbital interactions that interconnect these two *charge transfer* processes from the point of view of their frontier orbital (HO and LU) representations. For simplicity from this point on we shall use the symbols D and A to represent an electron donor and an electron acceptor, respectively, in any electron transfer step. In an energy transfer step, *R is always an energy acceptor, but in a photoinduced electron transfer step *R may be an electron acceptor (eA) or an electron donor (eD). With this notation consider the two basic steps (Eqs. 7.1-7.2) of positive hole and electron transfer which are represented by the orbital interactions shown in Figure 7.1a [Closs, 1989 #14]
Figure 7.1a. Frontier orbital representation of positive hole (top) and electron (bottom) transfer as elementary steps of charge transfer.

In Eq. 7.1, $A^+$ (Fig. 7.1a, top) can be considered as analogous to the orbital situation for which the electronic characteristics of only the half filled HO of *R emphasized. This emphasis views $A^+$ as a positive charge or electronic “hole” which is seeking a single electron to neutralize, i.e., by taking an electron from the HO of some electron, D In Fig. 7.1a (bottom) $D^-$ may be viewed as analogous to the half filled LU of *R, which is seeking a positive charge or hole to neutralize or LU to occupy. These electron transfer processes will be plausible only if the overall steps in Eqs. 7.1 and 7.2 are overall exothermic in terms of total free energy. We will describe how to determine how to compute and estimate the free energy changes in electron transfer processes in Section XX.

$$A^+ + D \rightarrow A + D^+ \quad \text{Positive Hole Transfer} \quad (7.1)$$

$$D^- + A \rightarrow D + A^- \quad \text{Electron Transfer} \quad (7.2)$$
For the energy transfer and electron transfer processes involving an electronically excited state (Scheme 7.1) we translate the paradigm into the D/A notation of Eq. 7.3 a-c.

\[
\begin{align*}
*D + A & \rightarrow D + *A \\
*D + A & \rightarrow D^+ + A^- \\
D + *A & \rightarrow D^+ + A^- 
\end{align*}
\]  

(7.3a) (7.3b) (7.3c)

Figure 7.1b illustrates how energy transfer and electron transfer processes involving *R can be viewed in terms of frontier molecular orbital interactions. These interactions are of the charge transfer type. In this description, the energy transfer process can be viewed conceptually as a sum of a synchronous electron and hole transfer (Figure 7.1b, top). We shall see that the accepted theoretical formulation of energy transfer by orbital overlap is described in terms of electron exchange which is at the initial stages of interaction is equivalent to partial charge transfer. We also note from Figure 7.1b (top) that the excited state of a molecule, *R, can be envisaged as the coexistence of an electron (half occupied LU) and a hole (half occupied HO) on the same molecule.[Atkins, 1991 #27]. In Fig. 7.1a the molecule, A^+, which possesses only a half occupied HO is considered an electron acceptor and the molecule, D^-, which possesses only a half occupied LU is considered an electron donor. *R which possesses a half filled HO and a half filled LU, can be considered both and electron acceptor and an electron donor. Because an electronically excites state simultaneously possesses a half filled HO (analogous to a positive hole) and a half filled negative LU (a high energy electron poised for donation), *R may serve as either electron donor (Figure 7b, middle) or as an electron acceptor (Figure 7b bottom). Whether *R will serve as an electron donor of acceptor will depend on the factors that
determine the exothermicity of the overall electron transfer process. These factors will be discussed in detail later in this chapter.

Figure 7.1b: Schematic relationship among hole, electron and energy transfer, based on the concepts in ref. [89Clo1]

Note that in Fig. 7.1a and 7.1b we have not assigned spin to the electrons; naturally we expect them to obey Pauli's exclusion principle. However, this still
leaves room for excited singlet and triplet states when two orbitals are singly occupied, i.e., one electron in a HO and one electron is a LU.

Now that we have described orbital interactions that can result in electron or energy transfer between *R and M once they have achieved a certain critical separation, we need to consider possible mechanisms for delivery of *R and M (which are assumed to start out at random separations in a solvent) to this critical distance. As an exemplar, let us consider the energy transfer process between *D and A (recall that in this case *R is always an energy donor, so we use the symbol *D to represent the excited state). The same delivery concepts will apply to electron transfer. In its simplest form the delivery process may involve diffusion through the solvent until *D and A "meet" at a distance suitable for transfer, i.e., come to a separation for which energy transfer can compete with deactivation of *D and with the separation of *D and A. In certain cases structural features may provide a "covalent spacer" that prevents diffusion and keeps *D and A at a fixed distance of separation. We will deal with questions of delivery later in this chapter. We cover initially the mechanisms by which electron or energy transfer can take place.

A number of processes may compete with energy or electron transfer. Again we use energy transfer as an exemplar. Eqs. 7.4-7.7 illustrate plausible steps which are competitive with energy transfer between an excited donor, *D, and acceptor A:
Among these plausible steps, only reaction 7.5, with rate constant \( k_{\text{ET}} \) leads to energy transfer (We shall use ET as a shorthand for energy transfer and eT as a short hand for electron transfer. Thus if we determine an experimental rate constant \( k_Q \) for "total quenching" of \(*D\) by \( A \) the value of \( k_Q \) will incorporate all modes of deactivation of \(*D\) by \( A \) as shown in Eq. 7.8.

\[
k_Q = k_{\text{ET}} + k_w + k_{\text{rxn}}
\]  

In Eq. 7.8, we use \( k_w \) to emphasize that in this step (Eq. 7.6) the energy is actually "wasted" relative to the desired energy transfer step. The efficiency of energy transfer, \( \phi_{\text{ET}} \), will be given by:

\[
\phi_{\text{ET}} = \frac{k_{\text{ET}} [A]}{k_D + k_Q [A]} = \frac{k_{\text{ET}} [A]}{k_D + (k_{\text{ET}} + k_w + k_{\text{rxn}}) [A]}
\]

The efficiency \( \phi_{\text{ET}} \) corresponds to the fraction of excited D molecules \(*D\) that decay via energy transfer (Eq. 7.5). \( \phi_{\text{ET}} \) differs from the quantum yield of energy transfer (\( \Phi_{\text{ET}} \)) in that the latter takes into account the quantum yield with which \(*D\) is formed \( \Phi_{*D} \) as given by Eq. 7.10.

\[
\Phi_{\text{ET}} = \Phi_{*D} \cdot \phi_{\text{ET}}
\]
In Eq. 7.10, $\Phi_D$ is the quantum yield for formation of $^*D$, for example, for intersystem crossing in the case of triplet states.

The quenching of $^*D$ by A does not necessarily require energy (or electron) transfer. Any of the bimolecular photochemical primary processes discussed in Chapter 6 will result in the “quenching” of $^*D$. The direct spectroscopic detection of $^*A$ usually implies energy transfer has occurred. However, the simple observation of $^*A$ but does not require ET to be efficient unless $\Phi_{ET}$ measurements confirm it.

The Trivial Mechanisms for Energy and Electron Transfer

We describe as "trivial" energy and electron transfer processes that involve mechanisms where the donor and acceptor act independently, just as if their reaction partner was not present, i.e., there is no electronic interaction between $^*D$ and A which “triggers” the transfer. Immediately one might ask, if there is no interaction between $^*R$ and M, how can electron or energy transfer occur at all? The answer is that $R^*$ may emit a photon (photoemission) or an electron (photoionization) without knowing of the existence of M, yet M may capture the photon or electron, resulting in a net overall energy or electron transfer between $^*R$ and M.

Thus, electronic energy transfer may occur in a "trivial" or radiative mechanism which consists of the emission of a quantum of light by the excited donor, $^*D$, which is followed by the absorption of the emitted photon by a ground state acceptor, A.[Birks, 1970 #64] This mechanism is readily understandable in terms of the principles that determine the efficiencies of light absorption and emission (see Chapter 4). The acceptor does not at all influence
the emission ability or emission probability of the donor molecule, whose excited state lifetime and other characteristics remains unchanged by the presence of A. The acceptor merely intercepts the photon once it has been emitted. Interestingly, in this case the delivery mechanism does not require a physical encounter of the participating molecules. Instead, it requires the photon to be emitted in certain direction and the medium to allow its transmission, i.e., in the case of energy transfer the medium should be transparent at the photon’s wavelength. The acceptor must meet some requirements related to absorption properties and orientation for the delivery to be successful. Indeed, in the case of trivial energy transfer, *D and A can be in different containers (Fig. 7.2)!

Thus, trivial radiative energy transfer occurs by the two-step sequence given in Eqs. 7.11 and 7.12.

*Mechanism of radiative emission-absorption energy transfer*

\[ *D \rightarrow D + h\nu \]  
(7.11)

\[ h\nu + A \rightarrow *A \]  
(7.12)
Figure 7.2: Trivial energy transfer between *D and A, with *A emitting following absorption of emission by *D. Part B emphasizes the independence of emission and absorption by noting that D and A could be in different containers. Color has been used to emphasize that emission from *A will be of lower energy than emission from *D.

The "trivial" mechanism requires that *D emits photons which A is capable of absorbing. In other words, the emission spectrum of *D must overlap the absorption spectrum of A. The rate or probability per unit time of energy transfer from *D to produce *A will depend on:

(a) The quantum yield ($\Phi_{eD}$) of emission by *D.
(b) The number of A molecules (concentration) in the path of photons emitted by *D.
(c) The light absorbing ability of A.
(d) The overlap of the emission spectrum of *D and the absorption spectrum of A, with consideration given to the extinction coefficient of A at the wavelength of overlap.

Trivial energy transfer will be favored when each of these parameters is maximized, while the process will fail completely if any one of the four criteria above is not met. Thus, the ideal conditions may involve $\Phi_e^D \sim 1$, high concentration of A, high extinction coefficient of A ($\varepsilon_A$) and good overlap of the emission spectrum of *D and the absorption spectrum of A. The last two factors may be quantified in terms of the spectral overlap integral, $J$, which is the integrated overlap of the experimental absorptions and emission curves (Figure 7.3). Note that while we normally represent spectra in terms of wavelength ($\lambda$), in this case it is necessary to calculate the overlap in terms of wavenumber, $\bar{\nu}$, i.e.:

$$\bar{\nu} = \frac{1}{\lambda}$$

(7.13)

Mathematically $J$ is given by:

$$J = \int_0^\infty I_\nu (\bar{\nu}) \varepsilon_A (\bar{\nu}) d\bar{\nu}$$

(7.14)

where $I_\nu$ is the emitted light intensity for the donor as a function of frequency, $\varepsilon_A$ the extinction coefficient of A. Both $\varepsilon_A$ and $I_\nu$ are functions of $\bar{\nu}$. 
Figure 7.3: Schematic representation of the overlap integral $J$ (see Eq. 14) and its relation to the experimental absorption and normalized emission spectrum of $^*D$ and absorption of $A$. (this overlap integral can be used for energy transfer also. See Fig. 9.3, p. 299 if MMP update)

Note that the value of the overlap integral $J$ in Eq. 7.14 will be very small if $\varepsilon_A$ is small independent of the degree of normalized overlap. Since values of $\varepsilon_A$ for direct singlet-to-triplet absorption are normally very small, it would be implausible for $^*A$ to be a triplet state; thus singlet-triplet and triplet-triplet energy transfer do not take place by the trivial mechanism.

By analogy with the case of energy transfer, we can envision trivial electron transfer mechanism by a similar two-step process, i.e., Eqs. 7.15 and 7.16.

*Mechanism of electron transfer by electron ejection-electron capture*

\[
\text{D} \quad \xrightarrow{\text{hv}} \quad \text{D}^+ + \varepsilon_{\text{solv}} \quad (7.15)
\]

\[
\varepsilon_{\text{solv}} + \text{A} \quad \xrightarrow{\text{h}} \quad \text{A}^- \quad (7.16)
\]
The mechanism of reactions 7.15 and 7.16 combine the “emission” or ejection of an electron to yield a “solvated electron”, \( e_{\text{solv}} \) in solution, with the capture of the electron by a suitable acceptor. The photoionization reaction (Eq. 7.15) may involve the absorption of one or more photons. In fact, two-photon ionization being quite common.\([\text{Piciulo, 1978 #65; Kawazumi, 1994 #66}]\) The photoionization process is generally more facile in polar media. In general, no bound state is expected to be involved in photoionization reactions as the excitation energy exceeds the first ionization potential. However, in the case of two-photon processes a bound state (e.g., the excited singlet or triplet states) may be involved and can absorb the second photon.

Solvated electrons can be readily detected in solution and are among the main species produced in the radiolysis of water.\([\text{Ben1}]\) For example, in aqueous solution they absorb with \( \lambda_{\text{max}} \approx 720 \text{ nm} \) and an extinction coefficient of \( \approx 20,000 \text{ M}^{-1} \text{ cm}^{-1} \).\([\text{Hug1}]\) One of their characteristic reactions involves scavenging by \( \text{N}_2\text{O} \), which is often used as a diagnostic test.\([\text{Ben1}]\)

\[
\begin{align*}
    e_{\text{aq}} + \text{N}_2\text{O} + \text{H}_2\text{O} & \rightarrow \text{N}_2 + \text{OH}^\cdot + \text{OH}^- \\
    (\lambda_{\text{max}} \approx 720 \text{ nm})
\end{align*}
\]

Solvated electrons are extremely reactive intermediates, and are readily trapped by the numerous organic and inorganic molecules which behave as electron acceptors. Oxygen, a very important molecule, (see Chapter 14) traps electrons with a rate constant of \( 2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \) in water at 25°C. Many organic substrates yield readily detectable radical anions when they trap an electron. Table 7.1 gives representative rate constants for several electron scavengers.
Table 7.1: Rate constants for the reactions of hydrated electrons with selected scavengers. In aqueous solution at 298 K.[92Ros1]

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$k \times 10^9$ M$^{-1}$ s$^{-1}$</th>
<th>Substrate</th>
<th>$k \times 10^9$ M$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inorganic</strong></td>
<td></td>
<td><strong>Olefins</strong></td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>20</td>
<td>styrene</td>
<td>3.0</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>9.0</td>
<td>tetracyanoethylene</td>
<td>15</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>39</td>
<td>butadiene</td>
<td>8.0</td>
</tr>
<tr>
<td><strong>Aromatic</strong></td>
<td></td>
<td><strong>Ketones</strong></td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>0.01</td>
<td>acetone</td>
<td>7.0</td>
</tr>
<tr>
<td>anisole</td>
<td>0.003</td>
<td>acetophenone</td>
<td>28</td>
</tr>
<tr>
<td>benzonitrile</td>
<td>19</td>
<td>benzophenone</td>
<td>28</td>
</tr>
<tr>
<td>naphthalene</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>acetonitrile</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>aniline</td>
<td>0.026</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Pyrene has been a frequent subject for photoionization studies to produce solvated electrons and the pyrene radical cation. The ejection of an electron is not limited to highly polar media; thus, two-photon ionization of pyrene occurs in water, alcohols and alkanes.[70Ric1,78Pic1]

A number of examples have been reported for which a molecule undergoes photoionization (normally as a two-photon process), and its ground state acts as a scavenger for the solvated electron. Acridine is a typical example where this occurs.[Kellmann, 1982 #25] In this system the acridine radical-anion eventually protonates to give a neutral radical.
7.3 Energy and Electron Transfer by Radiationless Mechanisms: Similarities and Differences

In addition to the radiative or "trivial" mechanisms presented in the previous section, energy transfer can take place by two distinct types of interactions between $^*\text{D}$ and A, that we will describe as dipole-dipole (also termed Coulombic, resonance or Förster) and orbital overlap (electron exchange) mechanisms. Sometimes the name of the individual who developed the theory is used. In this case exchange energy transfer is termed “Dexter” energy transfer and dipole-dipole energy transfer is termed “Förster” energy transfer. The terms dipole-dipole, Coulombic and Förster to describe energy transfer which corresponds to the interactions shown in Fig. 7.4 top and the terms orbital overlap, exchange and Dexter are used to describe energy transfer which corresponds to the interaction shown in Fig. 7.4 bottom. We already had a brief encounter with the interactions resulting from orbital overlap in Chapter 6 and in the discussion of orbital interactions of Figure 7.1.
In Figure 7.4 we make a schematic comparison of the behavior of the electrons in the HO and LU for these the dipole-dipole (Fig. 7.4, top) and exchange (Fig. 7.4 bottom) mechanisms of energy transfer.

![Figure 7.4: Comparison of the dipole-dipole and exchange mechanisms of electronic energy transfer.](image)

For bookkeeping purposes, we imagine that we can label the electrons which are interacting as electron 1 and electron 2 in Fig. 7.4. A key difference between the two mechanisms of Figure 7.4 is that when the interaction which triggers energy transfer is dipole-dipole in nature, the electrons do not "change molecules or orbitals", but rather two transitions (*D → D and A → *A) occur
simultaneously. The excitation of A to *A is exactly analogous to the mechanism for absorption of light in Chapter 4. In this case the electromagnetic field provides the oscillating electric dipole field. The oscillating electric field produced by *D is shown schematically in Fig. 7.4 below the orbital diagram. The excited molecule *D thus serves as “virtual photon” for the production of *A. Since no electrons are actually transferred between orbital in the dipole-dipole mechanism, it is clear that this dipole-dipole process cannot have an analogy in the case of electron transfer. That is, there cannot be electron transfer if electrons are not exchanged between donor and acceptor.

In contrast, in the case of the electron exchange mechanism there is a direct analogy between energy and electron transfer. In fact, as shown in Figure 7.1, energy transfer can be viewed as the sum of electron and hole transfers. In Fig. 7.4, to emphasize that electron exchange has occurred the electrons labeled 1 and 2 are shown as exchanging orbitals. In this mechanism orbital overlap is required and is shown schematically below the orbital diagram (Fig. 7.4 bottom).

We can relate the possibilities and rate constants for energy transfer, \( k_{ET} \), in terms of the corresponding Hamiltonian for the electron exchange and Coulombic interactions, given by Eq. 7.20.

\[
k_{ET} \text{ (total)} = \alpha \left[ \langle \Psi(D^*)\Psi(A) | H_e | \Psi(D)\Psi(A^*) \rangle \right]^2 \]

\[
= \text{Electron exchange} + \beta \left[ \langle \Psi(D^*)\Psi(A) | H_e | \Psi(D)\Psi(A^*) \rangle \right]^2 \]

\[
= \text{Electron dipole - dipole interactions} \tag{7.20}
\]

That is, the overall probability can be viewed as the sum of probabilities (or rates) for the two processes. We will now discuss the two mechanisms for energy transfer separately.
7.4 Visualization of Energy Transfer by Dipole-Dipole Interactions: A Transmitter-Antenna Mechanism

The dipole-dipole interaction between *D and A illustrated in Figure 7.4 (dotted arrows, dipolar electric field about *D) represents an "action at a distance", i.e., the electrons initially on *D stay on D, while the electrons initially on A stay in *A. In other words, the dipole-dipole resonance interaction *DA→Hdd→D*A (see Eq. 7.20 and dotted arrows in Figure 7.4) occurs via the interactions of the electromagnetic field of the oscillating dipole, *D with the electrons of A. This interaction does not require physical contact of the interacting partners. The basic mechanism involves the induction of a dipole oscillation in A by *D, just as the oscillations of the electromagnetic field of light induce a dipole transition in a molecule as light absorption occurs.

The dipole-dipole interaction represents a classical Coulombic interaction between charged particles, so that that a classical analogy is possible. Importantly, essentially the same result is obtained from a quantum mechanical approach (by analogy, two ‘point’ dipoles).[51For1] The electric field near an electronically excited molecule is assumed to behave like a field generated by a classical oscillating electric dipole whose frequency of oscillation is ν and whose instantaneous transition dipole (Chapter 4) is μ (Fig. 7.4 top). If |μ₀| is the maximal value of the induced dipole that can be achieved, to determine the value of μ at any instant we apply Eq. 7.21

\[ μ = μ₀ \cos (2\pi ν t) \] (7.21)

where t is the time. In molecular terms we can identify this oscillating dipole moment as the result of back-and-forth motion along molecular framework of
the excited electron on *D. Classically, for the ground state of A, the electrons are assumed not to be oscillating at all. The resulting dipolar electron charge oscillation of *D will cause the excitation of electronic systems of nearby molecules if certain resonance conditions are met. This dipole-dipole coupling mechanism, the "Förster mechanism" is only plausible in singlet-singlet energy transfer because only multiplicity-conserving transitions have large transition dipoles. Thus, whenever we find an example of triplet energy transfer we can readily rule out dipole-dipole interactions as implausible as a mechanism for energy transfer since neither the donor *D, nor the acceptor A possess significant transition dipoles.

For the Förster mechanism or any mechanism to lead to successful energy transfer a resonance condition (\(\Delta E = 0\), coupling interactions) must occur and *D and A must be coupled by the dipole-dipole interaction. For light absorption leading to *A, the resonance condition is given by Eq. 7.22 and the coupling is the result of the dipole-dipole interaction of the electromagnetic field and the electrons of A.

\[
\Delta E (A \rightarrow ^*A) = \hbar \nu \tag{7.22}
\]

For energy transfer the resonance condition is given by Eq. 7.23 and the coupling is due to the dipole-dipole interactions (of the correct frequency) of the oscillating dipole on *D with the electrons of A.

\[
\Delta E (^*D \rightarrow D) = \Delta E (A \rightarrow ^*A) \tag{7.23}
\]

We see a clear similarity between the absorption of a photon by A to produce *A and dipole-dipole energy transfer from *D and A to produce *A: in the case of light absorption (Eq. 7.22), the coupling occurs between the electrons of A and the oscillating electric field of the light wave and in the case of energy
transfer, the coupling occurs between the electrons of A and the oscillating electron of *D. Eq 7.23 reflects the requirements for both the resonance condition (initial and final states of equal energy) and for energy conservation (overall energy change for process must be equal to zero). While the excited state energies of donor and acceptor will usually be different, other modes will be required so that energy conservation is maintained; for example vibrational and rotational modes of the donor and acceptor may be recipients of some of the energy. In solution these species will usually reach thermal equilibrium rapidly by interaction with the solvent.

Förster Theory of Dipole-dipole Energy Transfer: Quantitative Aspects

The above discussion has provided some insight to the qualitative features of the Förster mechanism for electronic energy transfer. Indeed it was Förster who first provided a quantitative description of dipole-dipole induced electronic energy transfer, and this is the reason his name is associated with the dipole-dipole mechanism. What are the factors that influence the Coulombic electrostatic interactions responsible for energy transfer from *D to A? According to classical theory[,,51For1] the electrostatic interaction energy, E, between two electric dipoles is directly related to the magnitude of the two interacting dipoles (µD and µA, eq. 7.21) and the distance between them (RDA) as shown in Eq. 7.24:

Electrostatic interaction energy

\[ E \propto \frac{\mu_D \mu_A}{R_{DA}^3} \]  

(7.24)

Förster[,,51For1] related µD and µA to the oscillator strengths, f, for radiative *D ↔ D and A ↔ *A transitions (Chapter 4). He was thus able to
quantify the dipole-dipole interaction energy in terms of \( f_D \) and \( f_A \), the measured oscillator strengths for the radiative transitions of D and A (see Chapter 4), which, being properties of real systems, include electronic, vibrational and spin factors. Thus, a poor vibrational of Franck-Condon factor or a change in multiplicity will lead to small interaction energy because poor Franck-Condon factors correspond to small transition dipole moments. Recall that oscillator strength is related to the inherent radiative lifetime and the extinction coefficient of a given transition (Eqs 3.x and 3.xx update). Förster showed that the rate of energy transfer \( k_{\text{ET}} \) by the dipole-dipole mechanism is related to the square of the interaction energy of Eq. 7.24, \( E^2 \), a dependence that is characteristic for systems involving weak interactions (see Golden Rule in Chapter 4). Förster showed that \( k_{\text{ET}} \) can be related to \( E^2 \) quantitatively through Eq. 7.25. In this expression the rate of energy transfer is seen to fall off, as the separation, \( R_{DA} \), between *D and A increases, by \( 1/R_{DA}^6 \).

\[
k_{\text{ET}(\text{Dipole - dipole})} \propto E^2 = \left( \frac{\mu_D \mu_A}{R_{DA}^3} \right)^2 = \frac{\mu_D^2 \mu_A^2}{R_{DA}^6} \tag{7.25}
\]

From Eq. 7.25, Förster theory predicts that \( k_{\text{ET}} \) for an energy transfer via dipole-dipole interactions will be proportional to:

(a) The square of the transition dipole moment \( \mu_D \).

(b) The square of the transition dipole moment \( \mu_A \).

(c) The inverse sixth power of the separation between *D and A (i.e. \( 1/R_{DA}^6 \)).

To make quantitative comparisons with experiment, Förster related the theoretical quantities of oscillator strength and transition dipoles to quantities
that could be directly measured. In Chapter 4 we have shown the relationships between the transition moments and experimental quantities (Eqs. 4.xx, update):

Thus,

\[
\mu_D^2 (D^* \leftrightarrow D) \rightarrow \int (\epsilon_D \text{ or } k_D^0)
\] (7.26)

\[
\mu_A^2 (A^* \leftrightarrow A) \rightarrow \int (\epsilon_A \text{ or } k_A)
\] (7.27)

where \(\int \epsilon\) is the integrated extinction coefficient of an absorption band and \(k^0\) is the radiative rate constant.

Since we are specifically considering an energy transfer process where \(D^* \rightarrow D\) and \(A \rightarrow A^*\), we select \(k_D^0\) and \(\int \epsilon_A\) as the experimental terms to replace the square of the transition dipole moments and obtain Eq. 7.28.

\[
k_{ET} (\text{Coulombic}) \rightarrow \frac{k_D^0 \int \epsilon_A}{R_{da}^6}
\] (7.28)

Finally, we recognize the spectral overlap requirement and consider the overlap of \(D^*\) emission with \(A\) absorption and obtain Eq. 7.29.

\[
k_{ET} (\text{Coulombic}) = \alpha \frac{\kappa^2 k_D^*}{R_{da}^6} J(\epsilon_A)
\] (7.29)

The term \(\alpha\) is a constant determined by experimental conditions such as concentration and solvent index of refraction. The term \(\kappa^2\) takes into account the fact that the interaction between two oscillating dipoles depends on the mutual orientation of the dipoles in space. For a random distribution of interacting dipoles, \(\kappa^2\) is a constant equal to 2/3. The term \(J(\epsilon_A)\) is similar to the overlap integral of Eq. 7.14 with the extinction coefficient of the acceptor (\(\epsilon_A\)) is included in the integration.
The Relationship of $k_{ET}$ to Energy-Transfer Efficiency and Separation of Donor and Acceptor

From Eq. 7.29 we anticipate that the rate constant of energy transfer induced by the dipole-dipole mechanism will be most favored for *D and A pairs such that:

(a) The *D → D and A → *A processes correspond to a large (spectral) overlap integral, $J$.
(b) The radiative rate constant, $k_D^*$, is as large as possible [$k_D^* = (\tau_D^*)^{-1}$].
(c) The magnitude of $\varepsilon_A$ is as large as possible.
(d) There is a small spatial separation between *D and A.
(e) There will be a preferred orientation for which energy transfer is most favorable.

Experimentally, the efficiency rather than the rate constant of energy transfer by the dipole-dipole mechanism is often measured, since the latter depends on the spatial separation $R_{DA}$ between *D and A (recall that $k_{ET} \propto 1/R_{DA}^6$). Conceptually, the efficiency tells us the fraction of decaying *D molecules that succeed in transferring energy to the acceptor A. It is convenient to define an efficiency for which the rate of energy transfer equals the sum of the rates of deactivation of *D as shown in Eqs. 7.30 and 7.31, $k_D$ is the reciprocal of the experimental lifetime of *D under the conditions of the experiment and at [A] = 0, not of the radiative lifetime.

$$k_{ET} [D^*] [A] = k_D [D^*]$$  \hspace{1cm} (7.30)

at $R_{DA} = R_{DA}^0$
or,

\[ k_{et} [A] = k_D = \tau_D^{-1} \quad (7.31) \]

Note that we use \( k_D \) and \( \tau \) to refer to the experimental rate constant for decay and lifetime of \( *D \). This lifetime will normally be shorter than the radiative lifetime \( \tau^*_D \) [recall \( \tau^*_D = (k^*_D)^{-1} \)]. The efficiency of emission from this state is related to these lifetimes by

\[ \phi_{\text{emission}} = \frac{\tau_D}{\tau_D^0} \quad (7.31a) \]

When \([A]\) is such that the equality of Eq. 7.30 holds experimentally we may calculate \( R_\circ \), for the average separation for \( *D \) and \( A \). \( R_\circ \) is termed the "critical separation" for which the rate of energy transfer and inherent rate of deactivation of \( *D \) are equal. Taking into account geometric factors and assuring spherical shapes for \( D \) and \( A \), the relationship between \( R_\circ \) and the concentration \([A]\) that meets the criteria of Eq. 7.30 is given by (see also Section zz update with cross reference to Perrin section):

\[ R_\circ \text{ (in Å)} = 6.5 \ [A]^{\frac{1}{3}} \quad (7.32) \]

(with \([A]\) in M units)

The rate constant and the efficiency for energy transfer by the dipole-dipole mechanism may be related to any actual separation \( R \) of \( *D \) and \( A \) by the expressions shown in Eqs. 7.33 and 7.34[.,51For1]

Rate constant for any separation:
Energy and Electron Transfer

\[ k_{ET} \propto k_D \left( \frac{R_o}{R} \right)^6 = \frac{1}{\tau_D} \left( \frac{R_o}{R} \right)^6 \]  

(7.33)

Efficiency for any separation:

\[ \phi_{ET} \propto \left( \frac{R_o}{R} \right)^6 \]  

(7.34)

where, \( \tau_D \) is the actual experimental lifetime of \( \*D \), \( R \) the separation between centers of \( \*D \) and \( A \), \( R_o \) the critical separation as defined above and \( \phi_{ET} \) is the efficiency for energy transfer (see Eq. 7.10). Thus, when \( R_o = R \) the rate of energy transfer equals the rate of deactivation (see Eq.s 7.30 and 7.31). When \( R < R_o \), energy transfer predominates, while when \( R > R_o \) deactivation of \( \*D \) dominates.

The *theoretical* critical separation \( R_o \) may also be calculated from an approximate equation, where the emission spectrum of the donor is expressed in terms of its absorption spectrum by using an assumed mirror image symmetry of these spectra.[51] Typical values of \( R_o \) are in the 10-50 Å range.[Birks, 1970] (Give a few experimental examples. From MMP?)

7.5 Electron Exchange Processes: Energy Transfer Resulting from Collisions.

We normally view bimolecular chemical interactions as occurring via *collisions* between reaction partners. By collisions we mean that the participants in the reaction are sufficiently close that their electron orbitals overlap significantly in space. In the region of orbital overlap electron exchange can occur. The processes of interest to us and that can occur by electron exchange include:

(a) Energy transfer in some cases (always in the case of triplet-triplet energy transfer)
(b) Triplet-triplet annihilation
(c) Charge transfer

We already saw in Figure 7.1 that energy transfer by the exchange mechanism can be viewed as the sum of electron and hole transfer processes. This may give the impression that energy transfer is an intrinsically more complex process that electron transfer; this is not necessarily the case. Charge transfer processes are frequently complicated by the involvement of the solvent in the process, a factor that any successful theory of electron transfer must take into consideration. In contrast, in the case of exchange energy transfer the solvent plays a less critical role, although diffusion is naturally important in the actual delivery of the energy from the donor to the acceptor. In this Section we will deal with energy transfer first and then with charge transfer later.

Energy Transfer by Electron Exchange: An Overlap or Collision Mechanism

If we approximate orbitals as spheres, then we can estimate the fall off of orbital overlap with separation and also the rate constant for energy transfer by electron exchange. As two spherical orbitals on \( D \) and \( A \) separate, the overlap between the orbitals is expected to fall off exponentially as the separation of \( D \) and \( A \) increases. This exponential fall off is characteristic of the distance dependence of orbital overlap. Since the rate of exchange energy transfer is directly related to the orbital overlap of \( D \) and \( A \), the rate constant for exchange energy transfer is expected to fall off as a exponential function of the distance separating \( D \) and \( A \). In addition to the dependence of the rate of exchange energy transfer on the separation of \( D \) and \( A \), the rate of energy transfer will also be directly related to
$J$, the spectral overlap integral, which is a measure of the number of states that are capable of satisfying the resonance condition, once $^*D$ and $A$ are coupled by the exchange interaction. A theory of energy transfer by electron exchange was worked out by Dexter,[Dexter, 1953 #67] who proposed for the rate constant of energy transfer is given by Eq. 7.35

$$k_{ET} \text{ (exchange)} = KJ \exp(-2r_{DA}/L) \quad (7.35)$$

where $K$ is related to the specific orbital interactions such as the dependence of orbital overlap to the instantaneous orientations of $^*D$ and $A$. $J$ is the normalized spectral overlap integral (see Eq. 7.14), where ‘normalized’ means that both the emission intensity ($I_D$) and extinction coefficient ($\epsilon_A$) have been adjusted to unit area on the wavenumber ($v$) scale. It is important that $J$, by being normalized does not depend on the actual magnitude of $\epsilon_A$. $r_{DA}$ is the donor-acceptor separation relative to their van der Waals radii, $L$. By being defined in this manner $r_{DA}$ corresponds to the edge-to-edge separation (by comparison, we use $R_{DA}$ for center-to-center). In comparing dipole-dipole (or Förster) interactions and Dexter (i.e., electron exchange or orbital overlap interaction) energy transfer processes, we note the following differences in their predictions.

(a) The rate of dipole-induced energy transfer decreases as $R^{-6}$ whereas the rate of exchange-induced transfer decreases as $\exp(-2r/L)$. Quantitatively, this means that $k_{ET}(\text{exchange})$ drops to negligibly small values (relative to the donor lifetime) as the intermolecular (edge-to-edge) distance increases more than on the order of one or two molecular diameters (5-10Å);

(b) The rate of dipole-induced transfer depends on the oscillator strength of the $^*D \rightarrow D$ and $A \rightarrow ^*A$ radiative transitions, but the rate of the
exchange-induced transfer is independent of the oscillator strength of the *D → D and A → *A transitions;

(c) The efficiency of energy transfer (fraction of transfers per donor lifetime \( \sim k_{ET}/k_D \)) by the dipole mechanism depends mainly on the oscillator strength of the A → *A transition (since a smaller oscillator strength for *D → D is compensated by a slower radiative rate constant) and is directly related to \( \Phi_D \), whereas the efficiency of energy transfer by the exchange interaction cannot be directly related an experimental quantity.

Both Förster and Dexter theories predict a direct dependence of \( k_{ET} \) on \( J \), the spectral overlap integral.

**Electron exchange processes leading to excited states**

The formation of excited states of *A via electron exchange can occur by way of two distinct electron transfer mechanisms. These are illustrated in Figure 7.5. The energy transfer involves a concerted two-electron transfer, in turn requiring good overlap between both HO of *D and HO of A, as well as between LU of *D and LU of A.
Figure 7.5: Mechanisms for forming D and *A via electron exchange processes. The conversion from the left to the center box corresponds to energy transfer, while those originating from the boxes on the right illustrate electron transfer where D acts as a hole donor (top) or an electron donor (bottom).

Excited states of *A can also be achieved via electron or hole transfer processes starting from radical ion pairs, as illustrated also in Figure 7.5. We will cover these types of transformations in more detail later on in this Chapter. We note however that charge separated structures as illustrated on the right may make some contribution to energy transfer if the two-electron exchange is not "fully concerted" i.e., if exciplex-like structures (see Chapter 4) are involved.

Triplet-Triplet Annihilation (TTA): a Special Case of Energy Transfer via Electron Exchange Interactions
In general, the energy gap between the lowest triplet state (T₁) of a molecule and its ground state (S₀) is larger than the singlet triplet (S₁ ↔ T₁) energy splitting, i.e.:

\[ E_{\text{triplet}} > \Delta E_{\text{singlet-triplet}} \quad (7.36) \]

This implies (see Figure 7.6) that in an encounter between two excited triplet states enough energy will be available to promote one of the molecules into the excited singlet state, provided the second molecule relaxes to the ground state. Thus, if we look at the encounter of two triplet *D molecules we have Eq. 7.37

\[ *D(T₁) + *D(T₁) \xrightarrow{k_{\text{TTA}}} *D(S₁) + D(S₀) \quad (7.37) \]

\[ \text{with} \quad \Delta H < 0 \]
Figure 7.6: The relative energy levels of S₁ and T₁ are usually such that two triplets carry enough energy to produce one molecule in the S₁ state.

Figure 7.7 provides an orbital description of an electron exchange of this type. Even at this pictorial level, we can expect that not all triplet-triplet encounters can lead to this process, since most of the time the spin configuration will not be suitable for the formation of two singlet states. The fraction of possible successful encounters is governed by spin statistics already discussed in Chapter 2, such that the following is expected:

(a) 1/9 will be singlet encounters capable of the electron exchange interactions required for the successful completion of the process of Eq. 7.37. Note however, that any process yielding two ground state D molecules will also be part of this group.

(b) 3/9 will be triplet encounters, capable of producing *D(T₁) + D(S₀). That is, this interaction represents a form of quenching for *D. Note that from the viewpoint of spin statistics a possible outcome would be *D(T₁) + *D(S₁); however, the energetics are unfavorable by ΔE_{singlet-triplet} and thus a highly improbable process.

(c) 5/9 will be quintet encounters. These are expected to be dissociative; as a consequence the two triplets separate after an unsuccessful encounter.
Figure 7.7: Pictorial representation of electron exchange interactions in triplet-triplet annihilation leading to $S_1$ formation. Only 1/9 of triplet-triplet encounters can have the correct spin configuration for this interactions to be possible, see text for discussion.

Analysis of the statistics and consequences listed in (a)-(c) leads to the conclusion that at most 1/9 of the encounters can lead to $^*D(S_1)$ and the maximum observable rate constant for events leading to net electron exchange processes would be 4/9 of the rate of diffusion control [i.e., (a) + (b)].

When $^*D(S_1)$ is capable of fluorescing with significant efficiency, the most evident experimental manifestation of TTA interactions in emission of long lived fluorescence. Note that even if $^*D(S_1)$ itself is very short lived, this state is populated via $^*D(T_1)$ according to Eq. 7.37, thus, the concentration of $^*D(S_1)$ will continue to be replenished for as long as $^*D(T_1)$ is present. The apparent lifetime of this long-lived fluorescence will be of the order of magnitude of the triplet lifetime, the actual value depending on what other forms of decay the triplet state
may be involved in. [Birks, 1968 #69; Parker, 1963 #68] TTA thus leads to a form of delayed fluorescence. This is often referred to as "P-Type" delayed fluorescence, to differentiate from the "E-Type" involving thermal population of the singlet state (see Chapter zz update).

We may suspect that under most experimental conditions the concentration of triplet states in solution may be very low. We may therefore wonder if a process requiring the encounter of two triplets and with a maximum probability of 1/9 will occur at all. Three key factors can make TTA a significant process in spite of those stringent requirements:

(a) The rate constants for TTA, \( k_{\text{TTA}} \), are generally very large (see Table 7.2 for representative values).

(b) Pulsed lasers are widely used in photochemical laboratories. With these light sources triplet state concentrations in excess of \( 10^{-5} \) M are common. Typical products \( k_{\text{TTA}}[^{\text{D}}(T_1)] \) may then be around or over \( 10^5 \) s\(^{-1} \). Thus, any triplet with lifetime of a few microseconds (a common situation) will undergo at least some TTA in fluid solution.

(c) The high sensitivity with which fluorescence can be detected makes TTA an easily observable process even when it is not the major mechanism for triplet decay.

Table 7.2: Representative rate constants for triplet-triplet annihilation (TTA) in solution.a

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Solvent</th>
<th>( T ), (K)</th>
<th>( k_{\text{TTA}} ) (( 10^9 \text{M}^{-1}\text{s}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene[,],88Sal1</td>
<td>toluene</td>
<td>258</td>
<td>2.74</td>
</tr>
<tr>
<td>Anthracene[,],88Sal1</td>
<td>toluene</td>
<td>298</td>
<td>4.10</td>
</tr>
</tbody>
</table>
1,2-Benzanthracene [Stevens, 1964 #70]

Pyrene [Bohne, 1990 #28]
- cyclohexane, room T, 7 ± 2
- dodecane, room T, 5 ± 1
- hexadecane, room T, 1.9 ± 0.2

* comments on $k_{TTA}$ vs. $2k_{TTA}$ to be added

7.6 Types and Energetics of Electron Transfer

Charge separation can have several manifestations in photochemical reactions. We have already covered in Chapter 4 examples of excimers and exciplexes, both of which have properties that reflect the separation of charge or charge shift between reaction partners. In this Section we will be concerned with cases where full electron transfer takes place either in the form of charge transfer between an excited state and a ground state, or electron or hole transfer between ground state species of different charge as shown in Eqs. 7.38-7.41.

\[
*D + A \rightarrow D^+ + A^- \quad (7.38)
\]

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

\[
*D + A \rightarrow D^- + A^+ \quad (7.39)
\]

Electron transfer

\[
D^- + A \rightarrow D + A^- \quad (7.40)
\]

Hole transfer

\[
D^+ + A \rightarrow D + A^+ \quad (7.41)
\]
Naturally, charge transfer does not necessarily require the involvement of an excited state (see Eq. 7.40 and 7.41), although in the context of this book this is the case of special interest.

Before we examine in detail the theory of electron transfer, it is important to establish if the reaction of interest is in fact possible from an energetic point of view. We have seen in Chapter 6 and in the above discussions that \( \text{R} \) (when \( \text{R} \) is a closed-shell molecule) is always a better oxidizing and reducing agent than \( \text{R} \). This is true for both excited singlet and triplet states. A simple and powerful basis for this generalization is presented in Figure 7.8. From this Figure we can conclude that:

(a) the electron affinity (EA) is larger for the excited state, \( \text{R} \), than for the ground state; i.e. more energy is released in going from the ionization limit to the HO, than from going from the ionization limit to the LU of any molecule.

(b) the ionization potential (IP) is lower for the excited state, \( \text{R} \), because more energy is required to remove an electron from the HO than from the LU.

This analysis leads to the remarkable generalization that \( \text{R} \) is both a better reducing agent (lower IP) and a better oxidizing agent (higher EA) than \( \text{R} \).
Figure 7.8: Orbital representation of oxidation and reduction processes for the ground and excited state.

The energies associated with Figure 7.8 refer to the gas-phase, where both the electron affinity and ionization potential are applicable. Similarly, the "vacuum" refers to the energy of a free electron. Thus, for the following simple ground state electron transfer reaction in the gas-phase, Eq. 7.42, the free energy change for ground state electron transfer, $\Delta G_{gset}$, is given by Eq. 7.43.

$$D + A \rightarrow D^{\bullet\bullet} + A^{\bullet} \quad (7.42)$$

$$\Delta G_{gset} = (IP)_D - (EA)_A \quad (7.43)$$
For an excited state, \( ^*D \), (Eq. 7.38), the value of \( \Delta G \) differs by the magnitude of the electronic excitation energy, \( E^*_D \). This energy can be used to do work on electrons and assist in moving them from orbital to orbital in electron transfer processes. Thus, for reaction 7.38 and 7.39 above, we have Eqs. 7.44 and 7.45 which take the excitation energy into account.

\[
\Delta G_{38} = (IP)_D - (EA)_A - E^*_D \quad (7.44)
\]

\[
\Delta G_{39} = (IP)_A - (EA)_D - E^*_D \quad (7.45)
\]

Eqs. 7.44 and 7.45 show quantitatively how charge transfer in the excited state, \( ^*R \), will be generally be more favorable than in the ground state, \( R \) (compare with Eq. 7.43) whether \( ^*R \) acts as an electron donor (Eq. 7.38) or acceptor (Eq. 7.39).

From above discussion of the relatively low IP and high EA of \( ^*R \), it is not surprising that from the point of view of organic photochemistry, we will frequently be interested in charge transfer processes in solution. To determine the energetics associated with these processes, we could follow two distinct approaches:

(a) We could calculate \( \Delta G \) for the gas phase reaction (e.g. Eq. 7.44 for reaction 7.38) and then correct \( \Delta G \) to take into account the solvation energies for all the participants (i.e. \( {^*D, ^*A, D, A, D^+\bullet \text{ and } A^-} \)) in the reaction.

(b) We could employ the electrochemical potentials for the oxidation of reductions involved to calculate free energy changes directly in solution.
While both approaches are valid, from the experimental standpoint, some of the parameters required for (a) are frequently unavailable. For example the dissolution energies for $^*D$ or $D^{+\cdot}$ (gas phase to solution) are not readily available from experiment. In contrast, for approach (b) the key electrochemical parameters are frequently available or can be determined using standard electrochemical techniques, such as cyclic voltammetry, so that this approach is most commonly used.

For in solution Eq. 7.44 transform to Eq. 7.46

\[ \Delta G_{38} = F E_D^{o+} \ln D - F E_A^{o-} - E_D^{o} \]  

where $F$ is the Faraday constant ($9.65 \times 10^4$ Coulomb/mol) and $E^{o(D+/D)}$ and $E^{o(A/A^{-})}$ are the corresponding electrochemical potentials for A and D, both expressed as reductions. The sign "≈" emphasizes that this is only an approximate expression. The two significant approximations which are commonly required for analysis of photochemical reactions involving charge transfer are:

(a) The term $E_D^{*}$ is normally an enthalpy, not a free energy. The difference is $-T \Delta S_D$ where $\Delta S_D$ is the excitation entropy for D. While this term is frequently neglected, it can be significant if extensive changes in conformational freedom occur upon excitation (see entropy discussion later in this chapter).[,,85Ges1,,93Zha1]

(b) There is a Coulombic energy gain associated with bringing the two nascent particles of opposite sign together. For reaction 7.38 where

\[ \text{Insolution :} \]

\[ \Delta G_{38} = F E_D^{o+} \ln D - F E_A^{o-} - E_D^{o} \]  

‡ Two conventions, using electrochemical potentials as oxidations or reductions are in use. The one used here is most frequently employed in North America.
two neutral molecules give an anion and a cation the Coulombic correction term is proportional to $-e^2/\varepsilon r$, where $e$ is the charge of the electron, $\varepsilon$ the dielectric constant of the solvent and $r$ the approach distance between $D^{+*}$ and $A^{-}$ and as a first approximation can be taken as the sum of the radii for the two anions.

For example, Scheme 7.1 shows an example taken from a classical paper by Rehm and Weller. [,,70Reh1] In this system the excited singlet state of naphthalene is quenched by 1,4-dicyclobenzene via electron transfer. All electrochemical potentials are for acetonitrile against a “standard calomel electrode”.

![Scheme 7.1](image.png)

$E(S_1) = 3.94$ eV $= 90.9$ kcal/mol

$$\Delta G = FE^{0}_{D^{+}/D} - FE^{0}_{A^{-}/A^-} - E^{0}_D - 0.2$$

$$\Delta G = 36.9 - 92.1 - 0.2 = -17.6 \text{ kcal/mol}$$

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

**Scheme 7.1:** Electron transfer between the excited singlet state of naphthalene (donor) and 1,4-dicyclobenzene as acceptor. Data corresponds to acetonitrile.[,,70Reh1]
The back reaction, to yield naphthalene and 1,4-dicyanobenzene, both in their ground state, is approximately 75 kcal/mol exothermic. This is a common situation, where forward electron transfer is favored in the excited state, but reverse electron transfer is heavily favored in the ground state. We will elaborate further on this aspect later in this chapter.

By introducing the Coulombic term mentioned above, Eq. 7.46 transforms to Eq. 7.47

\[
\Delta G_{38} = FE^{o}_{D^*/D} - FE^{o}_{A/A^*} - E^{*}_{D} - N_A \frac{e^2}{4\pi \varepsilon_0 \varepsilon r}
\]  (7.47)

where \( N_A \) is Avogadro’s number, \( e \) is the charge of the electron (1.60 \( \times 10^{-19} \)C), \( \varepsilon_0 \) the permittivity of vacuum (8.85 \( \times 10^{-12} \) C² N⁻¹ m⁻¹), \( \varepsilon \) the dielectric constant of the solvent and \( r \) the distance between the two charges. We can refer to the last term in Eq. 7.47 as the "Coulombic term".

\[
\text{Coulombic term} = N_A \frac{e^2}{4\pi \varepsilon_0 \varepsilon r}
\]  (7.48)

\[
= \frac{331.5}{\varepsilon r} \text{ (in kcal/mol with } r \text{ in Å)}
\]

Figure 7.9 shows the magnitude of the Coulombic term for representative solvents with dielectric constants ranging from 2.27 (benzene) to 80.2 (water).
Clearly the Coulombic term will be very small (for example compared with $E_D^*)$ in polar solvents. For example, in water the Coulombic term is less than 1 kcal/mole at separations of only 2 Å. In contrast in non-polar solvents the term may become sufficiently large to favor ionic association, rather than dissociation. For example, in benzene, the Coulombic term is about 10 kcal/mole at a separation of 2 Å. These values should be compared to the average kinetic energy of a molecule at room temperature, which is ca. 1 kcal/mole. Note that if ions separate completely ($r \to \infty$) then the Coulombic term is zero. However, when we calculate $\Delta G$ for electron transfer processes, we may be interested in the free energy change associated with the nascent ions, which are within several Å or less of one another, even if some or all of these may eventually separate to infinity.
Now that we have covered the reasons why excited states, $^*R$, are both better electron donors and acceptors than the corresponding ground states, $R$ (see Figure 7.8) and that we know how to evaluate the free energy changes associated with electron transfer processes, we can deal with the theories that allow us to understand electron transfer.

### 7.7 Marcus Theory of Electron Transfer

At first glance an electron transfer would appear to be the simplest chemical reaction of which one could conceive. In an electron transfer reaction no bonds are formed or broken: the only thing that happens is that an electron "changes its owner", i.e., moves from one orbital to another. In spite of its apparent simplicity, electron transfer processes have challenged experimental and theoretical chemists for many decades and is of fundamental importance in many biological and industrial systems. By far the most important “application” of photoinduced electron transfer occurs in nature in the process of photosynthesis.

We have referred to the importance of polarity of solvent in electron transfer reactions. The modern theory of electron transfer may be traced to a seminal paper published in 1952, in which Libby[Libby, 1952 #71] pointed out the importance of “solvent reorganization” in controlling the rates of electron transfer reactions in the ground state. For example, when an electron donor molecule $D$ (solvated) converts to $D^{++}$ (solvated) the solvation spheres of $D$ and $D^{++}$ must change reflecting the rearrangement of the solvent molecules (dipoles) around the nascent electrical charge which is being created about $R$ (a similar situation applies to the electron acceptor that is formed in the electron transfer
process). Even in a simple charge translocation between identical particles, the solvent spheres need to reorganize (Eq. 7.49)

\[
R^+ + R \rightarrow R + R^*
\]  

(7.49)

How can we tell that reaction 7.49 has actually occurred? Isotopic labeling of \(R^+\) and \(R\) permits an easy distinction between otherwise identical reagents and products.

Libby assumed that electron transfer would be a much faster process than molecular bond and vibrational or solvent reorganization, the latter structural changes would follow the transfer of the electron. Marcus followed up Libby’s theory and pointed out that if molecular and solvent rearrangements followed electron transfer, then energy requirements would correspond to the vertical transition (\(\lambda\)) or otherwise would violate the principle of energy conservation (see Fig. 7.10). In other words, Marcus proposed that the rate limiting feature of an elementary electron transfer process requires the molecules and solvent to reorganize themselves for electron transfer to occur. Once the reorganization of the molecular and solvent structures have taken place, the electron transfer is fast. Marcus’ insight brings up the important issues: What is the nature and what is the magnitude of the reorganizational energy changes required to prepare a system for electron transfer? In other words, what is the nature and the energy required to reorganize the reactants and the solvent so that they are “prepared” for the electron transfer event? These reorganizations of the reactant and solvent can be conceptually divided in two types, termed inner sphere and outer sphere reorganization. These terms derive from Libby’s original paper which dealt with metal ions for which the term “inner sphere” refers to the ligands which are directly bonded to the metal ion.
complex and “outer sphere” refers to the shell of solvent molecules which solvate the complex. In Marcus’ theory, for organic molecules, the term inner sphere refers to the internal coordinates of the reactants and products (i.e., bond lengths and angles), while outer sphere refers to coordinates defining the arrangements of solvent molecules around the reactants and products.

Figure 7.10: An identity reaction showing electron transfer as a stepwise process is which electron transfer occurs without any solvent rearrangement, which follows as a distinct step. The different shapes illustrate the different solvation (and perhaps molecular structure) for R and R⁺. The colors is used as a marker to help us follow each species as electrons are exchanged; while we cannot ‘color’ our molecules and ions as we study these processes experimentally, isotopic composition can be used as a marker. Marcus recognized the problems with this interpretation and proposed an alternate theory.

In the case of reaction 7.49 we may imagine that R⁺ may be somewhat smaller than R because the positive charge causes a contraction of the electron cloud about the ion. This is a common situation with inorganic ions (e.g.,
Fe(H₂O)₆²⁺ is larger than Fe(H₂O)₆³⁺, but to some degree is also expected to be true for organic molecules. Further, some internal bonds and angles will be different in R⁺ and R. The solvent molecules (which we assume to have a significant dipole moment) will be largely oriented randomly around R if it is a non-polar molecule. However, significant organization about R is expected if R has a significant dipole moment. In the case of R⁺ the dipoles of a polar solvent will be ten to be oriented with their negative end towards R⁺. Thus, we can visualize reaction 7.49 for a non-polar organic molecule as follows (Fig. 7.11). The solvent will be randomly oriented around the R molecule but highly organized around R⁺.

![Diagram](image)

**Figure 7.11:** Visualization of the *inner* (note size change) and *outer* (note solvent reorganization) changes accompanying reaction 7.49.

Based on the idea of inner and outer sphere reorganization, Marcus was developed a model for electron transfer which allowed the computation of the *energies associated with the inner and outer sphere reorganization*. If the computation of the *reorganization energies* are possible, the experimentalist not only has great predictive power concerning the rates of electron transfer processes, but also is provided with a simple visualization of the process and a
series of predictions that can be easily put to the test. For example, the rate of a cross reaction \((X^{n+} + Y^{m+} \rightarrow X^{(n+1)} + Y^{(m-1)+})\) was predicted to be directly related to the rates of self reactions; i.e. to electron exchanges such as that of Eq. 7.49.

A basic assumption of Marcus theory\[\text{[,,59Mar1]}\] is that only a weak electronic interaction of the reactants is needed for a simple electron transfer process to occur. Marcus theory relates electron transfer to the concepts of reaction rate theory, potential energy surfaces and ion solvation in a familiar way. For example, we can start with the well known Arrhenius type expression (Eq. 7.50) which the rate constant of an electron transfer process \((k_{et})\) to an activation energy \(\Delta G^\ddagger\) and a frequency factor: 

\[
k_{et} = \nu_N \kappa \exp\left(-\Delta G^\ddagger/RT\right)
\]

In Eq. 7.50, \(\Delta G^\ddagger\) is the free energy of activation for electron transfer, \(\nu_N\) the electronic factor, effectively determining the maximum possible value for \(k_{et}\), and \(\kappa\) the transmission coefficient. \(\kappa\) has the same significance as in transition state theory, i.e. is the probability that the reactants, once they reach some critical arrangement of inner and outer coordinates, will successfully proceed to products. The significance of the various terms in Eq. 7.50 can be visualized for a reaction with \(\Delta G = 0\) in Figure 7.12 in which the energy curve of the reactants is represented by the parabola on the left and the energy curve of the products is represented by the parabola on the right. We recognize these curves as parabolas of a harmonic oscillator. We shall see that the approximation of the energy curves are parabolas allows for a powerful use of geometry to make some


\[\text{Note the use of the subscript "et" (lower case) for electron transfer, and "ET" (upper case) for energy transfer. This convention is employed throughout this Chapter.}\]
remarkable predictions concerning the rate constants of energy transfer reactions as a function of the inner and outer sphere reorganization energies involved in the overall reaction.

Figure 7.12: Potential energy description of an electron transfer reaction with $\Delta G = 0$. The point $\dagger$ represents the transition state.

Note that in Figure 7.12 $\Delta G^\dagger$ represents the free energy requirement to reach the transition state configuration (TS$^\dagger$) from the minimum of the reactant potential energy curve. The reactants (R) need to reorganize both internally and externally to meet the requirements for electron transfer to be possible. Once TS$^\dagger$ has been reached some systems will proceed to the product (P) surface, while others will be formally "reflected" and return to the reactants at this point. The transmission coefficient $\kappa$ gives us the probability that the reorganization required
to reach $\text{TS}^\dagger$ will be followed by movement along the product surface and the corresponding relaxation.

In Fig. 7.12, a parabolic potential energy curve of the reactant $R$ is shown as intersecting a parabolic potential energy curve of the product. The potential energy curves represent the equilibrium free energy of the reactant and product for a thermally neutral reaction as a function of some coordinate for the reorganization of the solvent. The solvent is assumed to reorganize its coordinates in a continuous fashion along the reaction coordinate. It is easy to imagine that the reaction coordinate also includes the coordinates of inner sphere reorganization. If the electron jumped from $R$ to $P$ without solvent reorganization representative point would move from the minimum of $R$ to the point of the $P$ curve which is vertically above that minimum (the same situation as in Figure 7.10). For a thermal neutral reaction (minima of $R$ and $P$ are at the same free energy), the energy required to make this vertical jump is defined as $\lambda$ and is equal to the reorganization energy required for an electron transfer to occur. We see that $\lambda$ corresponds to the reorganization energy that is required to “prepare” the reactants for the electron transfer step. Thus, $\lambda$ corresponds to the vertical separation, at the reactants equilibrium geometry, between the reactant and products curve for an isoergonic reaction ($\Delta G = 0$). Note that $\lambda$ is the energy barrier that needs to be overcome in order to transfer the electron without any prior reorganizations, as in the hypothetical example of Figure 7.10; Libby's original model for electron transfer would correspond to this situation.

The difference between the Libby and Marcus theories are illustrated in Figure 7.13. In the Libby theory the representative point is assumed to pay a steep energetic price in jumping from the reactant curve to the product curve vertically first and then passing on to product. In the Marcus theory, the representative point pays a much lower energy price by reorganizing the molecular structure
and the solvent structure along the reaction coordinate and then passing from R to P at the surface crossing, where the free energy of the system is the same whether the electron is on the reactant or the product. Note that even for reactions where $\Delta G \neq 0$, the parameter $\lambda$ is still defined with reference to the isoergonic situation.

![Potential energy curves comparison](image)

**Figure 7.13:** A comparison of the free energy requirements of the electron transfer pathways in the Libby and Marcus models.

As a reaction becomes increasingly exergonic, the values of $\Delta G^\ddagger$ change to reflect the vertical displacement of the reagent (R) and product (P) energy curves. Figure 7.14 shows the evolution of the potential energy curves as this displacement occurs:
Figure 7.14: According to Marcus theory as the product curve (P) moves down ($\Delta G^\circ$ becomes more negative) the activation energy first decreases, then becomes zero (in C) when the intersection coincides with the minimum in the reactant (R) curve, and eventually $E_a$ increases again as $\Delta G^\circ$ becomes more negative; This is the Marcus inverted region.

Inspection of the behavior of the two potential energy curves of Fig. 7.14 leads to a remarkable and very non-intuitive prediction. Under the assumption that the reaction coordinate does not change significantly with reaction exothermicity:

(a) first the barrier to electron transfer ($\lambda$) decreases as the reaction becomes more exothermic;

(b) a situation is reached for which there is no barrier to reaction when the potential curve for P passes through the minimum of the potential curve for R;

(c) as the reaction becomes more exothermic beyond (b) a barrier to electron transfer occurs and increases monotonically with increasing exothermicity.

Thus, the free energy of activation, $\Delta G^\dagger$ is initially expected to decrease as $\Delta G^\circ$ becomes more negative, until the product curve intersects the reagent curve at its
minimum (curve C in Figure 7.14). Thus, in the A-C region the rate increases as $\Delta G$ decreases, as we would intuitively expect. However, past this point (curves D) $\Delta G^\ddagger$ increases as $\Delta G^\circ$ become more negative. Thus, this simple scheme would predict that the rate constant of an electron transfer reaction would decrease as it becomes more energetically favorable in the region between C-D in Figure 7.14. This is known as the Marcus inverted region, and was predicted by Marcus\[,,60Mar1\] based on his theory of electron transfer.\[,,56Mar1;,,59Mar1\] We shall see some striking verification of this remarkable prediction of Marcus theory in the following section.

The conclusions made from the pictorial series of curves shown in Fig. 7.14 can be made quantitative through Marcus’ theory.

From the assumption of simple parabolas to represent the energy curves of R and P, from the geometric properties of parabolas, Marcus was able to relate the reorganization energy, $\lambda$, to the activation free energy of reaction by Eq. 7.51.

$$\Delta G^\ddagger = \frac{\lambda}{4} \left(1 + \frac{\Delta G^\circ}{\lambda}\right)^2$$ (7.51)

For an isoergonic reaction (as in Figure 7.12) Eq. 7.51 reduces to Eq. 7.52.

For $\Delta G^\circ = 0$

$$\Delta G^\ddagger = \frac{\lambda}{4}$$ (7.52)

Thus, the thermoneutral condition ($\Delta G^\circ = 0$) allows a definition of $\lambda$, the reorganization energy in terms of two intersecting parabolas. Marcus used plane geometry to connect $\lambda$ to the experimental rate constant for energy transfer, $k_{eT}$, (which is related to $\Delta G^\ddagger$ by the Arrhenius expression) and then relating $\Delta G^\ddagger$ to $\lambda$. 
Figure 7.14b shows the effect of free energy and reorganization energy on the value of the free energy of activation. Note the use of a reverse scale in the vertical axis in order to retain the usual appearance or Marcus-type curves. The $\Delta G^\ddagger$ values that intersect the vertical line at $\Delta G^0 = 0$ correspond to $\lambda/4$, as given in equation 7.52.

![Figure 7.14b: Plot of the free energy of activation ($\Delta G^\ddagger$), according to equation 7.51 for various values of the reorganization energy ($\lambda$). Note how the condition for $\Delta G^\ddagger = 0$ (the maximum of the curve) moves to the more exergonic region when the value of $\lambda$ increases.](image)

A second important limiting case occurs when the reaction is exothermic and $|\Delta G^0| = \lambda$. Since the free energy is a negative number for exothermic reactions, the value of $\Delta G^0/\lambda = -1$. From inspection of Eq. 7.51, when $\Delta G^0/\lambda = -1$, the value of $\Delta G^\ddagger = 0!$ This corresponds to the maximum of each curve in Figure 7.14b. Taking Marcus theory at face value we have two valuable connections between the rate of electron transfer and the reorganization energy. The two situations for which $\Delta G^0 = 0$ and for which $|\Delta G^0| = \lambda$ for an exothermic reaction are included in Fig. 7.14 as cases a and c, respectively.
Thus, in summary, simple geometric considerations and the application of the ideas of Fig. 7.12 allow the connection between the theoretical quantity $\lambda$, the reorganization energy for electron transfer, and the activation free energy for electron transfer. Since the activation free energy of a reaction is related to the rate of a reaction through Eq. 7.50, we can relate $\lambda$ to $k_e$. These remarkable relationships (see Figure 7.12) are a direct geometric consequence of the use of harmonic oscillator (parabolic) functions to describe the dependence of $\Delta G^\circ$ on the nuclear coordinates. Thus, from Eq. 7.51, for $-\Delta G^\circ > \lambda$ the activation free energy will increase as $\Delta G^\circ$ becomes more negative.

Let us take a close look at the horizontal axis in Figures 7.12 and 7.14 and ask what does the reaction coordinate actually represent? While the reaction coordinate is usually pictured in a rather qualitative fashion, it can indeed be accurately defined for a given reaction. In essence it provides a simplified way of representing in two-dimensions the evolution of many internal coordinates of the system in their progress from reactants to products. During this evolution the change in inner coordinates of the reactant must be accompanied by an adequate change in the structure of the solvent (i.e. the outer coordinates).

What is the significance of the crossing points of the potential curves representing the R and P? According to Marcus[,,59Mar1] "in this atomic configuration, a hypothetical system possessing the electronic wave function (and therefore the ionic charges) of the reactants must have the same energy as that of a hypothetical system possessing the electronic wave function of the products in the same configuration".

Given that the curves in Figures 7.12 and 7.14 reflect changes in both inner and outer coordinates, we can anticipate that the value of $\lambda$ will be determined by contributions from the same origin, i.e.:

$$ \lambda = \lambda_{\text{inner}} + \lambda_{\text{outer}} \quad (7.53) $$
Both contributions can be independently evaluated if sufficient information is available on the system of interest.

The value of $\lambda_{\text{inner}}$ will reflect the significant changes (e.g. in bond orders) between the structures of the reactants and the products. Examination of reactant and product structures can therefore provide an intuitive idea of the magnitude of $\lambda_{\text{inner}}$. The parameter can be evaluated accurately using Eq. 7.54.[,86Kav1]

$$\lambda_{\text{inner}} = \sum_i \left( \frac{f_i^R f_i^P}{f_i^R + f_i^P} \right) \Delta q_i$$

(7.54)

where $\Delta q_i$ is the change in interatomic distance and $f_i$ the force constant for the $i$th vibration. Typically values of $\lambda_{\text{inner}}$ will be between zero and a few kcal/mol. It is common to express the values in units of eV.

The outer reorganizational energy can be estimated as:[,56Mar1;,,59Mar1]

$$\lambda_{\text{outer}} = e^2 \left( \frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{AD}} \right) \left( \frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right)$$

(7.55)

$$r_{AD} = r_A + r_D$$

(7.56)

where $r_A$ and $r_D$ are the atomic radii, $\varepsilon_{op}$ is the dielectric constant of the medium that responds to the electronic polarization ($\varepsilon_{op}$ is the square of the refractive index), and $\varepsilon_s$ is the static dielectric constant or relative permittivity corresponding to the solvent dipole. Values of $\lambda_{\text{outer}}$ are typically a few tens of kcal/mol (most frequently $\lambda_{\text{outer}} < 40$ kcal/mol).

The expressions given above for $\lambda$ assume a dielectric continuum model for the solvent and a harmonic oscillator model for the vibrational terms.
Thus, typical values of $\lambda$ may be a few tens of kcal/mol. Recall however that it is $\lambda/4$ that affects directly $\Delta G^\ddagger$; thus, for $\lambda \sim 30.0$ kcal/mol (1.30 eV), $\Delta G^\ddagger$ for the isoergonic reaction would be 7.5 kcal/mol and lower for most exergonic reactions. $\Delta G^\circ$ would have to be more negative than $-60$ kcal/mol (see Eq. 7.51) in the inverted region before $\Delta G^\ddagger$ exceeds $\lambda/4$.

**Experimental Verification of the Marcus Inverted Region**

Marcus's prediction of the existence of an inverted region where increasing driving force leads to decreased reactivity,[56Mar1,59Mar1,60Mar1] posed a major challenge to experimentalists. Many results indicated that $k_{et}$ typically increased with increasing driving force, as expected intuitively, but as the driving force became very large, the values of $k_{et}$ reached a limiting value: that of a diffusion controlled reaction.

Rehm-Weller here

This meant that either the inverted region for electron transfer did not exist or that it was masked by rate limiting diffusion. If the latter was the case it meant that once the rate of electron transfer became diffusion controlled, one was measuring only the rate of diffusion, not of electron transfer. This is illustrated qualitatively in Figure 7.14c showing the effect of the diffusional rate constant on the experimentally observed value. In general the experimental value blends gently the two regions (as shown in the curved section), rather that simply result of the minimum of the two possible rate constants.
Figure 7.14c: The graph illustrates how the experimental rate constant is limited by the diffusion rate constant in the solvent, and as a result 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.

The problem of diffusion limit illustrated in Figure 7.14c frustrated many attempts to verify the Marcus inverted region. Thus, a key to finding experimental examples of the inverted region required a strategy which avoided the problem of diffusion controlled limiting reaction.

A successful strategy was developed by Closs and Miller, who designed the study of intramolecular, rather than intermolecular electron transfer processes, where diffusional effects tend to mask the true dependence of $\Delta G^\ddagger$ on $\Delta G^\circ$. When an electron transfer reaction is limited by diffusion kinetic analysis of rates of quenching of $^*R$ measure the rate of diffusion, not the rate of electron transfer. Thus, when electron transfer (or any) reactions become diffusion controlled (as in the example of Scheme 7.1) the expected differences in $k_{et}$ are lost, since $k_{diff}$ is the only parameter controlling the observed rates. For this reason intramolecular processes, where diffusion is not required, are a better way to test Marcus’ theory.
In order to avoid the problem of diffusion control of electron transfer reactions, Closs, Miller and coworkers [Closs, 1986 #38; Closs, 1988 #37; Miller, 1984 #36] used a rigid hydrocarbon spacer (Sp) based on the steroidal 5α-androstane moiety to separate the donor (D) and acceptor (A), i.e.:

\[
\text{A–Sp–D}
\]

The reaction studied was a charge translocation, following capture of a radiolytically generated electron by D (Eq. 7.55) in the A-Sp-D system, that is, this classic example is not a photochemical reaction. The process followed was the electron transfer from a donor (a biphenyl moiety) to a range of electron acceptors, A.

\[
\text{A–Sp–D} + e^- \rightarrow \text{A–Sp–D}^- \quad (7.57)
\]

\[
\text{A–Sp–D}^- \xrightleftharpoons[k_{et}]{-} \text{A}^- \text{Sp}–\text{D} \quad (7.58)
\]

Figure 7.15 shows the results of this classic study for eight different acceptors. The calculated curve corresponds to \( \lambda_{\text{inner}} = 0.45 \) eV and \( \lambda_{\text{outer}} = 0.75 \) eV. For \(-\Delta G^\circ\) values in excess of \( \approx 1.2 \) eV (\( \approx 27.7 \) kcal/mol) the rate constant decreases with increasing driving force, as predicted by Marcus theory. Note that in electron transfer studies it is common to express \( \Delta G \) values in units of eV. The conversion to other units of energy frequently used is:1 eV = 23.06 kcal/mol = 96.48 kJ/mol.
Figure 7.15: Intramolecular electron transfer rate constants (see Eq. 7.58) as a function of $\Delta G^0$ in methyltetrahydrofuran solution at 206 K. Reproduced with permission from the copyright owner (Closs, G. L.; Calcaterra, L. T.; Green, H. J.; Penfield, K. W.; Miller J. R., J. Phys. Chem. 1986, 90, 3673).

The variations in rate constants of almost four orders of magnitude are reduced to just a factor of four when the same electron transfer processes are studied as intermolecular reactions (Ref). Interestingly, Marcus[.82Mar1] predicted that the chance of seeing the inverted region in linked systems, where the transfer would be unimolecular, should be greater than in the case of bimolecular reactions. While the inverted region was part of the theories of
electron transfer since the 1950s, the work by Closs and Miller incorporates this concept into the experimental paradigm of electron transfer reactions.

Since the observation of Figure 7.11 was reported, numerous examples both intra and intermolecular which demonstrate the existence of an inverted region in other electron transfer processes have been reported. A few of these are presented later in this Chapter.

**GIVE EXAMPLES OF PHOTOINDUCE REACTIONS IN THE INVERTED REGION.**

We should realize that the Marcus inverted region represents a dramatic deviation from the concepts employed in typical free energy relationships in physical organic chemistry, where a monotonous dependence of rate constant and free energy change is usually expected. Interestingly, the inverted region is conceptually related to the energy gap law for internal conversion that we discussed in Chapter 5 and where the rate constant also decreases as the energy gap ($S_1 \rightarrow S_0$) increases. The Frank-Condon factors that are responsible for this effect are a reflection of the need for nuclear coordinates to change to accommodate an electronic change, just as they need to adapt to electron transfer changes (see Figure 7.12 and 7.14).

**Examples of photoinduced electron transfer which demonstrate the Marcus theory**

See the paper by Closs and Miller in Science. Add their examples, van Hoeven, Australian group, Gould and Farid in solution.

**Chemical Spectroscopy: Application of Marcus Theory to the Interpretation of Electron-Transfer control of Product distributions.**
In Chapter zz (Check) we already introduced chemical spectroscopy as a method to use photochemical reactions to measure the properties of excited states. Similarly, here we use the same concepts to understand electron transfer processes in organic photoreactions.

It is important to see that rates of electron transfer can influence not only the dynamics of a reaction, but also the final outcome in terms of products and their distribution. Amongst various examples which have been recognized over the last few years we will discuss the photochemistry of benzylic esters, a representative example reported by DeCosta and Pincock.[DeCosta, 1989 #72] Photolysis of a series of 1-naphthylmethyl esters, NME, yields products resulting from homolytic and heterolytic cleavage.

![Scheme 7.2](image)

| NMEA | X = H          |
| NMEb | X = 4-CN       |
| NMEc | X = 3-CH₃O     |
| NMED | X = 4-CH₃      |
| NMEe | X = 4-CH₃O     |
| NMEf | X = 4-C₂H₅     |
| NMEg | X = 4,8-(CH₃)₂ |
| NMEh | X = 4,7-(CH₃O)₂ |

Scheme 7.2 shows the process that takes place upon irradiation of NMEa-NMEb.
In this system \( k_R >> k_i \), so that the caged radical ion pairs are formed via the electron process indicated \( k_{et} \). Since \( k_{CO_2} \) is known or can be estimated (\( k_{CO_2} \approx 4.8 \times 10^9 \text{ s}^{-1} \)),[DeCosta, 1989 #72] it is possible to determine \( k_{et} \) from the product ratios as shown in Eq. 7.59.

\[
\frac{k_{et}}{k_{CO_2}} = \frac{\text{Yield } \text{Ar CH}_2 \text{ OCH}_3}{\text{Yield } \text{Ar CH}_2 \text{ CH}_2 \text{ Ph}} \quad (7.59)
\]

These rate constants can in turn be plotted as a function of the free energy change for the reaction (Figure 7.16) to yield the typical bell shaped curves reflecting both the normal and inverted regions discussed before.
**Figure 7.16:** Plot of \( \log k_{et} \) versus \( E^* \) of electron transfer for the conversion of the radical pair to the ion pair. The curve is a fit according to the Marcus Theory using \( \lambda = 0.39 \text{ eV} \). Reproduced with permission from the copyright owner from *J. Am. Chem. Soc.* 1989, 111, 8948.

In this system the free energy charge can be calculated as indicated in Eq. 7.47, which in this case corresponds to:

\[
\Delta G_{et} = FE_{(ArCH_2^*/ArCH_2^*)}^o - FE_{(PhCH_2CO_2^-/PhCH_2CO_2^{eq})}^o + N_A \frac{e^2}{4\pi \varepsilon_0 \varepsilon_r} \]

(7.60)

where the term \( E_{sp} \) has been omitted, since this is a ground state reaction. The Eq. can be simplified to Eq. 7.16,

\[
\Delta G_{et} = FE_{(ArCH_2^*/ArCH_2^*)}^o + B
\]

(ee.61)
which reflects that the only change along the series is in the substituent in ArCH₂, and B incorporates all of the other terms. Figure 7.16 has therefore been plotted as a function of $E^*$, a common practice in studies of this type. The system provides a clear example of how electron transfer can control product distribution (see Eq. 7.59) according to the Marcus Theory.

### 7.8 Contact and Solvent Separated Radical Ion Pairs

The analysis shown in earlier Sections suggests that the energetic terms associated with electron transfer have a strong dependence on the distance between charges (see for example Eqs 7.47 and 7.55). One could easily conceive that nascent radical ion pairs (e.g., reaction 7.38) may have different initial constitution depending on the nature of the reactions that generate them. For example, D and A may be able to form a ground state complex and electron transfer may occur following excitation of this complex, i.e.:

$$
D + A \xrightarrow{hv} D,A \rightarrow D^+ ,A^- (7.62)
$$

We may see here that the partners in the initial radical ion pair, $D^+,A^-$, may be very close, with no solvent molecules between $D^+$ and $A^-$. We describe this as a Contact Radical Ion Pair, or "CRIP".

Alternatively, the "same" radical ion pair could be formed by excitation of D, diffusion of the partners together and only then, electron transfer. Depending on the driving force, solvent, etc., the reaction could occur only when the partners are within contact distance, or while at least one solvent molecule still separates the partners. The two situations are illustrated in reactions 7.63 and 7.64, where (S) represents a solvent molecule located between the donor-acceptor pair. The
electrostatic interactions involved in each case will be different, and controlled by equation 7.48, following a similar dependence to that shown in Figure 7.9.

\[ \text{eqn 7.63} \]

\[ \begin{align*}
* \text{D} + \text{A} & \underset{\text{CRIP}}{\longrightarrow} * \text{D}(\text{S})\text{A} \quad * \text{D}, \text{A} \longrightarrow \text{D}^+, \text{A}^{-} \\
& \text{SSRIP} \\
\end{align*} \]

Thus, the product of reaction ee.64 is a Solvent Separated Radical Ion Pair (SSRIP) (sometimes represented by \( \text{D}^+/\text{A}^- \)), distinct from the CRIP formed in reaction 7.63. As is frequently indicated, the solvent molecules, (S), effectively "shield" the charges \( \text{D}^+ \) and \( \text{A}^- \), this shielding effect being highest in polar solvents (see Figure 7.9). By comparison the effects are not nearly as large with neutral molecules, where only minor effects (e.g. due to dipolar orientation) can be expected.

Given that ground state charge transfer complexes usually have absorption bands well resolved from those of D and A, it becomes straightforward to selectively excite the complex, separately from D and A. On the other hand, excitation of free D (even in complex-forming systems) can be achieved by either taking advantage of spectral differences, or by adequately reducing concentrations to shift the complexation equilibrium towards free D and A.

Yabe and Kochi[,,92Yab1] have examined in detail the ion pairs formed by photolysis of ground state complexes between tetranitromethane (A) and anthracenes substituted at the 9-position (D), i.e.:
In this system Yabe and Kochi were able to evaluate the key thermochemical and kinetic parameters relating to the behavior of the contact ion pair formed by excitation of the ground state complex. Is there an example closer to the exemplar reactions discussed in the aromatics chapter?

We also use Eq. 7.65 to illustrate the two types of nomenclatures currently in use.

\[ \text{D, A} \xrightarrow{k_1} \text{CRIP} \xrightleftharpoons[k_{-2}]{k_2} \text{SSRIP} \]  

Alternate nomenclature

\[ \text{D, A} \xrightarrow{k_1} \text{D}^+ / \text{A}^- \xrightleftharpoons[k_{-2}]{k_2} \text{D}^+ / \text{A}^- \]

In dichloromethane at room temperature for the parent anthracene (Y = H) \( k_1 = 9 \times 10^8 \text{ s}^{-1}; k_2 = 9 \times 10^8 \text{ s}^{-1}; k_{-2} = 4.3 \times 10^7 \text{ s}^{-1} \) and \( \Delta G_2 = 1.8 \text{ kcal/mol} \), where \( \Delta G_2 \) corresponds to the conversion between CRIP and SSRIP. The value indicates that CRIP is more stable than SSRIP. \( k_2 \) values were largely insensitive to the detailed structure of Y, but \( k_1 \) values changed between 3 \( \times 10^8 \text{ s}^{-1} \) (Y = CH₃) and 3.6 \( \times 10^9 \text{ s}^{-1} \) (Y = NO₂). Values of \( k_1 \) are also strongly dependent upon the solvent; as expected charge recombination is faster in non-polar solvents. Thus, for Y = H, \( k_1 \) changes from 9 \( \times 10^8 \text{ s}^{-1} \) in dichloromethane to 7.1 \( \times 10^9 \text{ s}^{-1} \) in benzene and >4 \( \times 10^{10} \text{ s}^{-1} \) in n-hexane.
In the case of CRIPs between substituted benzene cations and nitric oxide values of $k_1$ are in the $10^8$ s$^{-1}$ range. These relatively slow values reflect that the reaction is approximately isoergonic and that the reorganizational energy of NO is rather high.

While for simplicity we write the ground state complex as yielding directly CRIP upon excitation (see Eq. 7.62) this can be viewed as a two-step process, where the initial excitation produces an unrelaxed (or Franck-Condon) CRIP that then undergoes a configurational rearrangement to the lowest energy configuration of CRIP. Mataga and coworkers have measured relaxation times ($\tau_d$) between 0.5 ps and 2 ps for CRIPs derived from reaction 1,2,4,5-tetracyanobenzene with benzene, toluene and mesitylene.

$$D,A \xrightarrow{hv} (\text{CRIP})_{FC} \xrightarrow{\tau_d} (\text{CRIP})_{\text{relaxed}} \quad (7.66)$$

The mechanism of equation 7.66 corresponds to the processes of Figure 7.16b. Note the offset in the nuclear coordinates parameter between the ground and excited states. In other words the two state have different relaxed geometries, as well as different vibrational frequencies (i.e., the parabolas have different width). Excitation leads to a Franck-Condon state that then relaxes. One cannot help noticing the similarity with Libby’s model of Figure 7.13. However, in the case of Figure 7.16b, there is no conflict with the paradigms of thermodynamics, since the necessary energy is supplied photochemically.
Figure 7.16b: Excitation and relaxation of a ground state charge transfer complex. Note the parallel with Libby’s model (Figure 7.13).

CRIPs and SSRIPs also differ in their electronic characteristics. Thus the electronic coupling between partners in CRIPs is higher than in SSRIPs. This difference can be around 2 orders of magnitude. On the other hand, the reorganizational energy in the smaller CRIP is lower than in SSRIP, an effect that is mainly due to the solvent reorganizational term ($\lambda_{\text{outer}}$).

CRIPs and SSRIPs are clearly transient species which under normal conditions will either collapse to the D,A pair, or separate into the free ions. If the D,A pair does not form a ground state complex the partners will in turn separate into free D and A. Similarly SSRIPs will also separate. We will later examine some of these processes in the context of cage effects. For the moment it is useful to have some idea of the separation kinetics for the radical ion pairs, i.e.:
Typical values for $k_{sep}$ are between $10^7$ and $10^9$ s$^{-1}$ [Masuhara, 1981 #73] [Arnold, 1995 #74]. The values are usually higher in the more polar solvents, but are not very sensitive to details of molecular structure, such as ring substitution.

**Comparison Between Exciplexes and Contact Radical Ion Pairs (CRIPs)**

We described earlier (see Chapter 4) exciplexes as excited state complexes stabilized by some charge-transfer interaction. From our earlier description of CRIPs it is clear that in this case the charge-transfer stabilization may involve close to full electron transfer. Gould and Farid [Gould, 1992 #91] describe a CRIP as equivalent to an exciplex or an excited CT complex in which charge transfer from the donor to the acceptor is complete. Radiative and non-radiative return electron transfer processes are spontaneous transitions in which the energy difference between the A,D pair and A$^-$,D$^+$ is dissipated into nuclear motions of A,D and the solvent or emitted as light. Thus, for pure CRIP fluorescence emission represents return electron transfer to regenerate the starting materials in a contact configuration. These may separate (true exciplex) or remain in contact depending upon the tendency of the pair to form ground state charge transfer complexes.

Let us now consider the case of a CRIP undergoing a radiative transition to the ground state contact pair D,A. This is illustrated in Figure 7.17 where the heavy lines represent the lowest vibrational levels of D,A and D$^+$,A$^-$ and the thin lines are low frequency modes relating largely to solvent motion; i.e. these lines are related to the same motions that determine $\lambda_{outer}$. While under most
conditions only the lowest vibrational state of CRIP will be active, in the case of the end state, D,A, other vibrational modes may participate. For simplicity we start with a hypothetical example where only the lowest vibrational level (ν = 0) of D,A is active.

![Diagram showing CRIP, D^+, A^- and D,A with low frequency modes and emission intensity as a function of frequency.]

**Figure 7.17**: Schematic representation of radiative back electron transfer from a CRIP to the ground state pair D,A, and (right) emission intensity as a function of frequency.

Each emission frequency in Figure 7.17 corresponds to a different energy, or different ΔG_f. The probabilities for each one of these combinations between low frequency modes of CRIP and low frequency modes of D,A will be given by the usual Marcus type of dependence, potentially with a "normal" and an "inverted" region. Thus, the emission spectrum at low frequencies (left half)
represents the normal region and the high frequencies the Marcus inverted region.[92Gou1;93Gou2]

In reality, other vibrational modes of D,A can be expected to be active, each one associated with a set of different solvent low frequency modes, as shown in Figure 7.18.

![Figure 7.18](image)

**Figure 7.18:** Radiative back electron transfer from CRIP to several vibrational levels (j) of D,A. Each vibrational level has a quasi-continuum of low frequency modes associated with it. The arrows illustrate a few possible transitions, but many of these are possible. Each vibrational level leads to an emissive curve similar to that in Figure 7e.17. These add up to give the overall emission illustrated by the heavy curve.[92Gou1]

Each Gaussian curve (light numbered traces) in Figure 7.18 represents a transition from the lowest vibronic level of CRIP to a vibronic level (identified by j) of A,D. Each of these is a Marcus-type curves and their sum gives the overall
emission intensity observed. Thus, it is interesting that each emission spectrum from a CRIP or exciplex represents a demonstration of Marcus electron transfer theory. (Interesting point. Elaborate with a few sentences)

We have not included in Figures 7.17 and 7.18 radiationless electron transfer from CRIP to D,A. These do occur and can be represented by horizontal lines from CRIP to upper solvent modes of D,A.

ee.9 Energy and Electron Transfer Equilibria

We have so far written our examples of energy and electron transfer as irreversible. Note that the cases of back electron transfer presented above do not reflect a reversible process, since normally the donor, originally an excited state, *D, is produced in the ground state, D. There are however examples where these processes, specially energy transfer, are reversible. These are presented here.

Energy Transfer Equilibria

For an energy transfer equilibrium to be established it is necessary to have concentrations and rate constants for energy transfer sufficiently fast that the dominant mode of decay of the excited states will be via energy transfer (reaction 7.70) and not by other processes such as first order decay (reactions 7.68 and 7.69) i.e.:
Thus, it will be necessary that:

\[ k_{ET}[A] > k_D \]  
 \hspace{1cm} (ee.71)

\[ k_{-ET}[D] > k_A \]  
 \hspace{1cm} (ee.72)

Given that \( k_D \) and \( k_A \) will frequently have values \( \geq 10^8 \) s\(^{-1}\) for excited singlet states,\(^\dag\) and that \( k_{ET} \) in fluid solvents will be \( 10^9 - 10^{10} \) M\(^{-1}\) s\(^{-1}\) in the exothermic direction and much smaller in the endothermic direction, equilibration between singlet states can be expected to be quite rare at the low concentrations frequently employed in photochemical experiments. Thus, while singlet state energy transfer equilibration in solution is possible, it is not probable. This situation may be quite different if chromophores are linked by some type of molecular spacer. In this case singlet energy transfer can be fast enough for equilibration to occur. (Examples?)

In contrast to the case of singlet states, intermolecular equilibration of triplet states can be readily achieved in a number of cases, since \( k_D \) and \( k_A \) values for unreactive triplets are frequently 3-4 orders of magnitude lower than for singlet states.

The energy transfer equilibrium constant will be given by:

\[ \text{There are a few exceptions to this criterium. Notably, for pyrene } k_D \text{ values of } 2.5-3 \times 10^6 \text{ s}^{-1} \text{ are common in organic solvents. Similarly, some azo compounds have remarkably long singlet lifetimes.} \]
\[
k_{\text{ET}} = \frac{[D][A^*]}{[D^*][A]} = \frac{k_{\text{ET}}}{k_{-\text{ET}}}
\] (ee.73)

The concentrations of ground states, [D] and [A] are normally known, while [*D] and [*A] can be readily determined by a laser flash photolysis, provided that the triplet-triplet absorption spectra of *D and *A are sufficiently different. Experimentally the concentration ratio [*A]/[*D] is monitored as a function of time. A constant ratio is indicative of energy transfer equilibration.[74Kir1] The free energy for energy transfer is related to the equilibrium constant by:

\[
\Delta G_{\text{ET}} = -RT \ln K_{\text{ET}}
\] (ee.74)

\(\Delta G_{\text{ET}}\) values are in turn related to \(\Delta H_{\text{ET}}\) and \(\Delta S_{\text{ET}}\) by Eq. 7.75.

\[
\Delta G_{\text{ET}} = \Delta H_{\text{ET}} - T\Delta S_{\text{ET}}
\] (ee.75)

The enthalpic change for the overall energy transfer step, \(\Delta H_{\text{ET}}\), refers to the energy minimum, i.e. the relaxed triplet energies from donor and acceptor. This contrasts with energies derived from radiative processes (emission or absorption) which refer to vertical of Franck-Condon transitions (see Chapter 4 and 5).

Since the reorganization energy changes in energy transfer are usually small, it is a common practice to assume that \(\Delta S_{\text{ET}} \sim 0\) and thus that

\[
\Delta G_{\text{ET}} \approx \Delta H_{\text{ET}}
\] (ee.76)
which in turn allows a direct comparison of energy from spectroscopic measurement (e.g. phosphorescence) and energy transfer equilibrium. This assumption is a reasonable one for molecules only when there is little change in shape or in the degree of conformational freedom. Notably, single poly-aromatic molecules, such as naphthalene of chrysene meet well this criterion. For molecules where considerable changes in conformational freedom take place upon excitation (e.g. biphenyl, which loses its internal mobility in the triplet state) the assumption of $\Delta S \sim 0$ breaks down.

For systems where the assumption of $\Delta S_{ET} \sim 0$ is not valid it is possible to obtain excitation entropies by studying the temperature dependence of energy transfer equilibrium.

For the naphthalene/chrysene system $\Delta S_{ET}$ (chrysene as donor) was measured as 0.04 gibbs/mol, as expected for two nearly rigid molecules. In contrast for benzophenone (donor) and biphenyl (acceptor) $\Delta S_{ET} = -1.8$ gibbs/mol,\cite{85Ges1} and for 4-methylbenzophenone and 4-methylbiphenyl $\Delta S_{ET} = -2.0$ gibbs/mol,\cite{93Zha1} indicating that biphenyl loses more entropy than is regained by benzophenone on triplet energy transfer. (Give values of $T \Delta S$ for room temperature in kcal/mole)
Using data of this type it is possible to construct an approximate scale for $\Delta S^{c\rightarrow D}$ values. Such a scale places the excitation entropies of naphthalene, benzophenone and biphenyl at ~0, −4.1 and −6.1 gibbs/mol. Clearly biphenyl loses its flexibility along the central bond upon excitation. This result is gratifyingly consistent with other data concerning the excited singlet state of biphenyl (REF).

Excitation entropies, Franck-Condon factors and Stokes shifts are all determined by closely interrelated factors which reflect structural differences between ground and excited states.

**Electron Transfer Equilibria in the Ground State**

(This sort of et has been discussed above in the Closs Miller systems) While not strictly the subject on this book, it is important to realize that there are numerous studies of electron transfer equilibration between ground state species. For example, we may think of the radical anion for D reacting with the electron acceptor A, i.e.:

$$D^\bullet + A \underset{k_{et}}{\overset{k_{et}}{\rightleftharpoons}} D + A$$  (ee.77)
Note that this is the same charge translocation of reaction 7.40, where we have simply emphasized that $D^\bullet$ and $A^\bullet$ are radical-anions (and therefore short-lived reaction intermediates).

The equilibrium constant for reaction 7.77 can be readily estimated if the corresponding electrochemical potentials are available, i.e:

$$E_{A/A^-}^0 - E_{A/A^-}^0 = \frac{RT}{F} \ln K_{ET}$$

(ee.78)

or, if the appropriate kinetic data are available:

$$K_{ET} = \frac{k_{et}}{k_{et}}$$

(ee.79)

The following example has been taken from the abundant literature available on the chemistry of superoxide, $O_2^\bullet$.\[73Pat1\]

$$
\begin{array}{c}
O_2^\bullet + \\
\text{H}_2\text{C} \text{CH}_3 \text{O} \text{CH}_3 \\
\text{H}_3\text{C} \text{CH}_3 \\
\rightarrow \\
\text{H}_2\text{C} \text{CH}_3 \text{O} \rightarrow \text{O}_2 + \\
\text{H}_2\text{C} \text{CH}_3 \\
\text{H}_3\text{C} \\
\end{array}
$$

$k_{et} = 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$; $k_{et} = 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; $K_{et} = 0.023$, at 22°C

Excited State Electron Transfer Equilibria

Expressions similar to Eq. 7.78 can also be written for electron transfer reactions in the excited state. For example, we can write the same Eq. we used in previous examples, but now written as a reversible process, i.e.:
\[ \text{D}^* + \text{A} \xrightleftharpoons[k_{et}]{k_{et}} \text{D}^{+\cdot} + \text{A} \quad \text{(ee.81')} \]

Eq. 7.46 already provides an estimate for \( \Delta G \), although it ignores entropic terms. A more accurate expression would include them, i.e.:

\[
\Delta G_{et} = F E^{o}_{(D^*/D)} - F E^{o}_{(A^*/A)} - \Delta H_{et} + T \Delta S^{o}_{et} \quad \text{(ee.82)}
\]

Note that \( \Delta S^{c}_{et} \) and not \( \Delta S^{e}_{et} \) should be used as long as reaction 7.81 occurs with spin conservation.

We normally do not observe energy transfer equilibration as shown in Eq. 7.81 (i.e. with the free ions). This is largely due to the fact that the back reaction to give the excited donor (\( k_{et} \)) is less favorable than back electron transfer to yield the ground state (\( k_{bet} \)), as illustrated in reaction 7.83.

\[ \text{D}^{+\cdot} + \text{A}^{\cdot} \xrightarrow[k_{bet}]{k_{bet}} \text{D} + \text{A} \quad \text{(ee.83)} \]

Thus, if \( k_{bet} \gg k_{et} \) equilibrium will not be established, and the equilibration of reaction 7.81, while plausible is improbable. Note that while reaction 7.81 may not be efficient enough for an equilibrium to be established, this is not to say that back reaction does not occur at all; in fact chemiluminescent ion recombination is a well known process and is briefly described in the following Section.

**ee.10 Chemiluminescent Ion Recombination**
There are a few situations where ion recombination in solution can lead to an excited state, as shown in Eq. 7.84.

\[
D^+ + A^- \xrightarrow{k_{et}} D^* + A
\]  

(7.84)

where \(D^*\) is an electronically excited state which may or may not be the same one from which the reactants were initially formed. These are examples of chemiluminescent reactions for which chemical energy of recombination is converted into electronic excitation energy (Ref to MMP).

In fact, we have already seen one such example in the schematic representation of ion recombination of Figure 7.5, as well as in Scheme 7.1. In the latter we noted that the back reaction between the radical ions from naphthalene and 1,4-dicyanobenzene was \(\sim 75\) kcal/mol exothermic. Clearly this is substantially more than the triplet energy of naphthalene \(\sim 60\) kcal/mol). Thus, triplet formation via back reaction in Scheme 7.1 would be possible.

Two factors may contribute to make this process a probable one, even if not necessarily efficient:

(a) When reaction to the ground state takes place in the Marcus inverted region, the smaller \(\Delta G\) change to the excited products may be kinetically preferred.

(b) A triplet radical ion pair can populate an excited triplet state of D or A, but formation of ground state products is spin forbidden.

Figure 7.19 illustrates case (a), where the curves have been drawn so that the activation required for the ground state (more exothermic reaction) is higher than excited state formation.
Case (b), involving triplet state formation was established by Weller and Zachariasse\[,,67Wel2\] many years ago in the reactions of several aromatic hydrocarbon anions (e.g. pyrene and anthracene) with Wurster's Blue (the cation from N,N,N',N'-tetramethyl-1,4-phenylenediamine).

Among the many systems where these effects have been characterized the pyrene-N,N-dimethylaniline has figured prominently. Here the excited states of pyrene (Py\(^*\)) are formed by reactions of its anion (Py\(^-\)) with the cation from dimethylaniline (DMA\(^+\)).\[,,78Wer1;,83Wel1\]

\[
\begin{align*}
\text{Py}^- + \text{DMA}^+ & \longrightarrow \text{^3Py}^* + \text{DMA} \\
\end{align*}
\]

**(Figure 7.19):** Potential energy curves for ion recombination (see reaction ee.84) leading to chemiluminescence. Note that ground state formation occurs in the inverted region.
Note that only the triplet state of pyrene is energetically accessible; formation of the singlet state (from which the ions were formed) would be endoergonic. The occurrence of reaction 7.85 is detected through the delayed fluorescence of pyrene, as shown in reactions 7.86 and 7.87.

\[ ^3\text{Py}^* + ^3\text{Py}^* \xrightarrow{k_{TTA}} ^1\text{Py}^* + \text{Py} \]  

(7.86)

\[ ^1\text{Py}^* \xrightarrow{} \text{Py} + h\nu \]  

(7.87)

Reaction 7.86 (i.e. triplet-triplet annihilation) is a very rapid process, as shown already in Table 2.

Reaction 7.85 occurs not only between free radical ions in solution, but also in linked compounds, where the process effectively involves a biradical or biradical zwitterion. Systems linked by long \( \text{CH}_2 \) chains are generally most efficient, i.e.[Tanimoto, 1987 #53; Weller, 1984 #52]

\[ \text{(CH}_2\text{n)}_\text{N}^{\text{CH}_3} \]

(6 \( \leq n \leq 12 \)

It is worth noting that the luminescence resulting from these systems, whether involving free ions or in linked molecules, is strongly magnetic field dependent.[Tanimoto, 1987 #53; Weller, 1984 #52; Weller, 1983 #51] The effect results from Zeeman splitting of the triplet sublevels that influences the rates of spin evolution. The origin of these effects is discussed in Chapter 3.
7.11 Role of Molecular Diffusion in Energy and Electron Transfer Processes in Solution

The preceding Sections provide us with a background on the possible types, characteristics and mechanisms for energy and electron transfer. A key factor determining which one of these, if any, will be effective from *R (where the * may refer to either D or A in a photoinduced process) is the mechanism for delivery from donor to acceptor. The delivery may take advantage of a molecular property such as a possible intramolecular link of covalent bonds between D and A (as in the chemiluminescent systems just described) or, like in the trivial mechanism, of the ability of D and A to release and capture the energy or electron. Quite frequently the supramolecular medium (e.g. the solvent) will play a role in determining the ability of D and A to migrate through the solution such that the delivery may actually take place.

In essence, we can divide these delivery processes into three groups:

1. Preorganized proximity of D and A. Which may include systems with two or more linked chromophores (D-Sp-A) or supramolecular systems where a host environment ensures the proximity of donor and acceptor (D---A). In nature the photosynthetic unit takes advantage of such an arrangement.

2. Diffusional processes which bring D and A into proximity. While transfer (energy or electron) requires proximity, the medium is such that allows enough mobility for reaction partners to approach each other. We can think of this case as one of material transport.

3. Conducting medium which can transport energy or charge. Where the medium (solvents, bonds, space) can transport either the electronic
excitation or the electron. The trivial mechanisms discussed earlier exemplify this case. We will also present an example of energy migration later on.

In this section we will be specifically concerned with Case 2; i.e., with the effect of intermolecular diffusion on energy and electron transfer processes. When D and A are bound together by a flexible link of covalent bonds, intramolecular diffusion of D and A into proximity may be possible. The details of this intramolecular process have the same qualitative characteristics as intermolecular diffusion with the quantitative difference being that the motion of D and a will be determined by the conformational dynamics of the flexible chain for the linked molecular system and by the random walk of a pair of molecules for the free molecular system.

While all processes between a donor (D) and an acceptor (A) will generally benefit from proximity between the reaction partners, in the case of electron exchange processes, these require that D and A approach within collision separations as long as case 3 does not apply. Whether the outcome of the interaction between D and A is energy or electron transfer is largely unimportant in connection with those diffusional processes that bring D and A within the necessary distance for interaction. For processes which are determined by electron exchange interactions typical separation of D and A will be of the order of 2-5 Å. As a benchmark, a benzene molecules size is ca 5 Å. As a result, we shall assume that for good efficiency, energy transfer and electron transfer D and A should be partners in a solvent cage or separated by at most one solvent
molecule (for typical small molecule organic solvents). Our analysis shall refer to energy transfer only for simplicity. It should be noted that in the cases of charged intermediates Coulombic attraction (or repulsion) can play a role in determining the dynamics of these processes. Since this case is more common for electron than energy transfer the two situations will be discussed separately.

A Simple Example Involving Energy Transfer Controlled by Diffusion

Our first example of the diffusional control deals with energy transfer between the case where \( *R = *D \) and \( A \), the ground state acceptor. The overall energy transfer process (the symbol \( D + A \) shall refer to two independent molecules) is shown in Eq. 7.88.

\[
D^* + A \rightarrow D + A^* \quad (ee.88)
\]

For our analysis, the following assumptions are made: reaction 7.88 is exothermic, and the lifetime of \( *D \) and concentration of \( A \) are such that \( *D \) sees a "random" distribution of \( A \) molecules in its immediate surroundings. We will see later that these assumptions are valid for typical situations in fluid solutions when the lifetime of \( *D \) exceeds \( 10^{-8} \) s and the concentration of \( A \) is less than 0.1 M.

At this point we need to discuss more precisely what we mean by an “encounter” and an “encounter complex”. When \( *D \) and \( A \) approach each through diffusion and come within a separation of 2-5 Å, because of their proximity, there is a probability that they will remain in the same region for certain period of time. So to speak the \( *D/A \) pair is “bonded” by the statistics of having diffused
into each other’s proximity. If *D and A diffuse even closer to one another and come into contact we have a special situation in which the pair is now in a solvent cage. We shall use the notation $D^*A$ to denote a pair of molecules in a solvent cage and the notation $^*D/A$ to denote an encounter complex where $^*D$ and A are separate by on (or several) solvent molecules. The following discussion will refer to situations for which $^*D$ and A have become partners ($D^*A$) in a solvent cage simplicity.

A successful encounter of $^*D$ and A will result in energy transfer (Eq. 7.88) through the following sequence of events:

(a) $^*D$ and A diffuse through the solution until they meet as collision partners in an encounter complex $D^*A$.

(b) Exchange interactions occur between $^*D$ and A in the encounter complex $D^*A$, and one of these interactions eventually leads to energy transfer and generation of a new encounter complex $D^*A^*$.

(c) The encounter complex $D^*A^*$ breaks up into free D + $^*A$.

Note that point (b) introduces the suggestion that when $^*D$ and A meet they do not undergo just one exchange interaction and separate, but rather multiple exchange interactions occur when an encounter complex is formed. This is due to the fact that for $D^*A$ the partners are surrounded by a solvent cage, which effectively keeps the collision partners together for a much longer time than they would spend together if they underwent a gas phase collision. The phenomena of multiple collisions between partners ($D^*A$) in a solvent cage is the cage effect. Cage effects will be discussed in more detail later. Cage effects are quite important in radical pairs undergoing a competition between spin evolution and escape; this is discussed in detail in Chapter zz.
Diffusional encounters always occur in competition with the spontaneous or induced decay of *D through some of the processes discussed earlier, such as emission, radiationless decay or chemical reaction. We treat all of these competing processes as a group occurring with an overall rate constant $k_D$, (Eq. 7.89)

$$D^* \xrightarrow{k_D} D$$

Note that all steps in Eq. 7.90 have been written as irreversible; this will therefore be a "true" example of diffusion controlled energy transfer, where every encounter between *D and A leads to successful energy transfer. The only requirement for the process to be efficient is that the concentration of A be such that essentially all of the *D molecules decay via energy transfer rather than by Eq. 7.89, i.e., Eq. 7.91 is valid.

$$k_{DIF} [A] >> k_D$$

We note, however, that not every collision between *D and A in a solvent cage ($D^*A$) need lead to energy transfer. All that is required is that energy transfer occur before the encounter complex dissociates irreversibly; i.e., energy transfer must occur in the duration of the "cage". This is illustrated in the sequence of Eq. 7.92.
Estimation of Rate Constants for Diffusion Controlled Processes

The value of $k_{\text{DIF}}$ can be readily estimated from the rheological properties of the solvent and of the molecules involved in the interaction. Eqs. 7.95 and 7.94 represent a simplified form of the Smoluchowski Eq., which is frequently employed to estimate $k_{\text{DIF}}$.

$$k_{\text{DIF}} = 4\, \rho \, N_A \sigma D \times 10^{-3} \quad (ee.93)$$

$$\sigma = r_A + r_D \quad (ee.94)$$

In Eq. 7.93, $N_A$ is Avogadro's number, $\sigma$ is the reaction distance, frequently taken as the sum of radii for the two reactants ($r_A$ and $r_D$ in Eq. 7.94), $D$ is the diffusion coefficient and is equal to the sum of the diffusion coefficients for $D$ and $A$ and the factor of $10^{-3}$ takes care of unit conversion (m$^3$ to liters). $D$ is very strongly dependent on the resistance to flow for a given solvent, a characteristic which is also reflected by the solvent's viscosity.

For large solute molecules moving among relatively small solvent molecules it is possible to estimate the diffusion coefficients, $D_A$ and $D_D$; for example, for $D_A$ from Eq. 7.95,

$$D_A = \frac{kT}{6\pi \eta r_A} \quad (ee.95)$$

where $k$ is Boltzmann constant and $\eta$ is the solvent viscosity. Assuming $r_A = r_D$ and combining Eq. 7.93 to Eq. 7.95 leads to Eq. 7.96,

$$k_{\text{DIF}} = \frac{8RT}{\alpha \eta} \quad (\alpha = 3000) \quad (ee.96)$$
which is normally referred as the Debye Eq.\[.,42Deb1\] and allows for an easy estimation of diffusion controlled rate constants based on just the viscosity of the solvent.

Viscosities are normally expressed in units of Poise; since this is a cgs unit it requires that the gas constant, \( R \), be expressed in the same units \( (R = 8.31 \times 10^7 \text{ erg/mol}) \).

(For the purposes of the text, the difference between 2000 and 3000 as a factor is probably too small to be elaborated) For the opposite case, of small solute molecules moving among large solvent molecules a value \( \alpha = 2000 \) generally gives a better estimate of \( k_{\text{DIFF}} \). Of special interest in photochemistry is the case of molecular oxygen, where \( \alpha = 2000 \) may lead to a better estimate of \( k_{\text{DIFF}} \). Eq. 7.96 is also inadequate for extremely small species, such as atoms. For example, in the cases of oxygen and fluorine atom values of \( k_{\text{DIFF}} \) based on Eq. 96 can be too low by as much as a factor of five.[Bucher, 1994 #76; Bucher, 1994 #77]

Table 7.3 gives a series of estimates of diffusion rate constants assuming \( \alpha = 3000 \). These should be taken as rough estimates, keeping in mind that the true diffusion rate constants depend on individual values of diffusion coefficients and of the approach distance \( \sigma \), properties that are not independent of the solute.
When actual diffusion coefficients and critical distances are known a better estimate of $k_{\text{DIFF}}$ can be obtained using Eq. 7.93. Figure 7.20 gives plots of

**Table 7.3**: Experimental Values of Viscosity and Calculated Values of $k_{\text{DIFF}}$ at 25 °C, with $\alpha = 3000$. (Replace with ranges of $k_{\text{DIFF}}$ since the differences for most of the entries are small. Possibly a graph? Are these experimental or computed?)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Viscosity (cP)</th>
<th>$k_{\text{DIFF}}$ (M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>0.24</td>
<td>$2.70 \times 10^{10}$</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.31</td>
<td>$2.09 \times 10^{10}$</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.98</td>
<td>$6.63 \times 10^{9}$</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.42</td>
<td>$1.55 \times 10^{10}$</td>
</tr>
<tr>
<td>Octane</td>
<td>0.55</td>
<td>$1.18 \times 10^{10}$</td>
</tr>
<tr>
<td>Isooctane</td>
<td>0.50</td>
<td>$1.30 \times 10^{10}$</td>
</tr>
<tr>
<td>Dodecane</td>
<td>1.51</td>
<td>$4.30 \times 10^{9}$</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>3.34</td>
<td>$1.94 \times 10^{9}$</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.55</td>
<td>$1.18 \times 10^{10}$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.20</td>
<td>$5.41 \times 10^{9}$</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>0.45</td>
<td>$1.44 \times 10^{10}$</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>19.90</td>
<td>$3.26 \times 10^{8}$</td>
</tr>
<tr>
<td>Water</td>
<td>1.00</td>
<td>$6.49 \times 10^{9}$</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.65</td>
<td>$1.00 \times 10^{10}$</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.59</td>
<td>$1.10 \times 10^{10}$</td>
</tr>
</tbody>
</table>

$^a$ cP = 0.01 Poise
expected values of $k_{\text{DIF}}$ for a common range of solvent viscosities. In general, when we talk about typical non-viscous solvents we mean:

$$0.2 \text{ cP} \leq \eta \leq 2 \text{ cP}$$

Thus, typical values for $k_{\text{DIF}}$ are in the $3 \times 10^9$ to $4 \times 10^{10}$ M$^{-1}$ s$^{-1}$ range. Note that viscosities are usually expressed in "centi-Poise", cP (1cP = 0.01 Poise). The Poise is the cgs unit of viscosity.

![Figure 7.20](image)

**Figure 7.20:** Calculated values of $k_{\text{DIF}}$ based on Debye’s Eq. (eq. 7.96) for a range of common viscosities.
Given that viscosities are temperature dependent, we also expect $k_{\text{DIF}}$ to show a temperature dependence as shown in Eq. 7.96. Over a limited temperature range $k_{\text{DIF}}$ usually follows well an Arrhenius-type of temperature dependence (see Chapter 8). Typical activation energies, $E_{\text{DIF}}$, for fluid solvents are in the 2-4 kcal/mol range, while the "A-factor" (or pre-exponential factor) is frequently around $10^{12}$ M$^{-1}$ s$^{-1}$. Representative Arrhenius plots of $k_{\text{DIF}}$ calculated using Eq. 7.96 are given in Figure 7.21 along with the parameters derived for each solvent. Note that the choice of the value of $\alpha$ in Eq. 7.96 influences only the pre-exponential or $A$-factor and not the activation energy.

**Figure 7.21**: Temperature dependence of the diffusional rate constants calculated with Eq. 7.96 ($\alpha = 3000$). The activation energies are given in kcal/mol and the pre-exponential factors ($A$ in units of M$^{-1}$ s$^{-1}$) as their logarithm, as common practice in chemical kinetics.

Experimental criteria for diffusion-controlled energy transfer processes usually fall into one or more of the following categories:
(a) The measured value of the experimental bimolecular rate constant, $k_{OBS}$, is close to that calculated with Eqs 7.93 or 7.96.

(b) The experimental value of $k_{OBS}$ is a function of $T/\eta$, as expected from Eq. 7.96.

(c) The value of $k_{OBS}$ is essentially invariant for quenchers of widely varying structure, i.e., its value is a property of the solvent and not of the detailed molecular structure of D and A.

(d) The values of $k_{OBS}$ for different quenchers reach a limiting value which corresponds to the fastest bimolecular rate constant measured for that solvent.

Examples of processes which are totally diffusion controlled energy transfer processes are rare. The most compelling experimental criterion for a true diffusion controlled process is probably a strict correlation of the rate constant for the process investigated with the solvent viscosity as expected from Eq. 7.96. Such an example have been provided by Birks et al.[] who observed that the rate constants for quenching of naphthalene fluorescence by biacetyl in solvents of viscosity ranging from 0.34 cP (hexane) to 17.2 cP (liquid paraffin) were largely proportional to $\eta^{-1}$. In this case, quenching is probably due to singlet-singlet energy transfer via a simple overlap electron-exchange mechanism. It can be concluded in this case that every encounter of *D and A leads to energy transfer. The data are consistent with a quenching range of ~11 Å for effective transfer. We note that although each encounter leads to quenching of *D, it may take more than one collision of *D and A to result in energy transfer.

Diffusion control is not limited to excited state processes. In fact, when spin statistical factors (see Chapter 2) are taken into account radical-radical reactions provide an excellent example of diffusion control (see below). Schuh
and Fischer[78Sch1] have shown that the self-reaction of tert-butyl radicals in non-hydroxylic solvents shows diffusion controlled behavior and also follows (within 0.5 kcal/mol) the activation energies expected for viscous flow. Several other radical-radical reactions are similarly "well behaved". [88Sal1]

Those reactions that "approach" but do not reach diffusion-control can be divided in two groups.

**Group 1:** Reactions where spin statistical factors determine which fraction of the encounters have the correct spin configuration for reaction. This situation is common in the case of triplet quenching by molecular oxygen (see Chapter zz).[88Sal1] A similar situation arises in the self-reaction of free radicals (see above), where only 1/4 of the encounters have the correct spin configuration for product formation. These systems behave as typical diffusion-controlled processes (e.g. in their temperature dependence), except that rate constants are a constant fraction of $k_{DIF}$.

**Group 2:** Cases where the first step in Eq. 7.90 can be reversible. The next Section discusses the latter case.

**Examples of Near Diffusion-Controlled Reactions**

The scheme of reactions 7.89 and 7.90 can be readily modified to include the possibility of reversible steps energy transfer process, i.e.

\[
D^* \quad \xrightarrow{k_{DIF}} \quad D
\]

\[
D^* + A \quad \xleftrightarrow{k_{DIF}} \quad D*A \quad \xrightarrow{k_{ET}} \quad DA^* \quad \xrightarrow{k_{DIF}} \quad D + A^*
\]
In this case the observable rate constant for reaction between *D and A is given by Eq. 7.99.

\[
    k_{\text{OBS}} = \frac{k_{\text{DIF}} k_{\text{ET}}}{k_{\text{DIF}} + k_{\text{ET}}} \tag{ee.99}
\]

Note that if \( k_{\text{DIF}} \ll k_{\text{ET}} \), then Eq. 7.99 reduces to the case discussed in the previous section where \( k_{\text{DIF}} = k_{\text{OBS}} \). All other situations will lead to \( k_{\text{OBS}} < k_{\text{DIF}} \).

If we assume that \( k_{\text{ET}} \) will be approximately independent of the solvent viscosity, then it is easy to see from Eq. 7.99 that a reaction that is not diffusion controlled in a low viscosity solvent, may become diffusion-controlled in high viscosity solvents, i.e., when \( k_{\text{DIF}} \ll k_{\text{ET}} \). We note that as the solvent becomes more viscous at the macroscopic level, the walls of the solvent cage hinder separation of the caged radical pair more. Effectively the lifetime of the pair *D/A increases, more collisions between *D and A in the solvent cage occur before separation of the pair, and the energy transfer step can approach or reach complete efficiency.

An example of the relationship of viscosity to the rate of energy transfer is illustrated in the example of Figure 7.22; in this case, the valerophenone triplet (\( E_T \sim 73 \text{ kcal/mol} \)) has been quenched by 2,5-dimethyl-2,4-hexadiene (\( E_T \sim 58 \text{ kcal/mol} \)). The measured \( k_{\text{OBS}} \) for triplet energy transfer is not a linear function of reciprocal viscosity for a series of inert solvents.[68Wag1] Note that the experimental rate constant approaches diffusion-controlled only for \( \eta \geq 2 \text{cP} \), in a range that we could regard as *viscous fluids.*
A common situation is one in which the activation energy for diffusion (see Figure 7.16) is higher than that of $k_{ET}$; in fact, for D–A pairs where energy transfer is more than 4-5 kcal/mol exothermic, $k_{ET}$ may be essentially temperature independent. Under these conditions the temperature dependence of $k_{OBS}$ will lead to an experimental activation energy which is lower than that for diffusion-control. Since $k_{DIF} > k_{OBS}$ and $k_{DIF}$ will change with temperature more than $k_{OBS}$, the two rate constants may "meet" at low temperature and under these conditions the process may become diffusion-controlled.

7.12 The Cage Effect
When two organic molecules diffuse together and "encounter" in the gas phase the two molecules are said to "collide elastically", that is to have no special binding. Their encounter therefore typically lasts for only a single collision that typically lasts about $10^{-12}$ s. The situation is different in solution. When two organic molecules encounter in solution and eventually become partners in a solvent cage, they find themselves in a "crowded environment". The "walls" of the solvent cage confines them for a certain period of time. As a result, the pair finds itself undergoing many collisions before succeeding in separating from the solvent cage. Effectively the solvent "walls" around this pair of molecules cause the pair to become correlated and "bounce" against the walls and each other many times before they find a "hole" in the solvent wall and can diffuse out and become solvent separated. In other words, the model of a solvent cage suggests that collision between encountering molecules in solution causes collisions to occur "in sets". The same solvents molecules that tend to hinder the encounter of two molecules in solution, also hinder their separation, thus leading to a "long lived" cage encounter. (Check Franck, Noyes papers)

Thus, we have a model that two molecules undergo only one collision in the gas phase, but can undergo many collisions in a solution solvent cage. The term employed to describe the effect of the solvent is the solvent cage effect. A pair of molecules can find themselves sharing a solvent cage after they undergo a random encounter, or because they were "born" together as a result of a chemical reaction (for example the fragmentation of a larger molecule); when the pair is born together we refer to them as a geminate pair. A classical mechanical experiment demonstrating the effect of confinement and crowding on collisions was performed by Rabinowitch and Wood,[36Rab1] who placed a number of balls in a star-shaped tray. Two balls (one fixed at the center of the tray and the
other a mobile one) were marked, and the collisions between this pair recorded as a function of time as the balls were allowed to roll by agitation of the tray. When they had very few balls on the tray (simulating the gas-phase) the collisions between the marked balls occurred as single events. Addition of more balls had no effect on the average frequency of collisions between the two marked balls, but their distribution in time changed dramatically. At higher concentration of the balls one has a model for the liquid phase. Under these conditions, collisions now occurred in groups. We now have a physical model for an encounter of two molecules in a liquid: when two molecules diffuse from random positions into a solvent cage and undergo multiple collisions, they are said to undergo an encounter. For example, when the percent coverage of the tray surface was 72 %, approximately 20 collisions took place during each encounter. The results of this interesting experiment are illustrated qualitatively in Figure 7.23. (GET BETTER ART OR DIRECTLY FROM PAPER).
Figure 7.23: Schematic representation of the collision frequency in the gas phase (A) and in solution (B). Note that the average number of collisions is the same in both cases (based on ref.[,,36Rab1] and the type of representation given in [,87Lai1]).

Even when reaction partners are separated by at least one solvent molecule, their local concentration is sufficiently high that the probability of a re-encounter can be 50%, thus leading to a new chance for reaction. This is called "secondary cage reencounter",[,88Gui1] and is due to the non-uniform distribution of reactants. This model of “inert” balls mechanically encountering each other is an appropriate model for *D and A undergoing energy transfer in a liquid. However, in studies of electron transfer it is important whether reaction partners are in *contact in a solvent cage or are separated by one or a few solvent molecules. We shall discuss in Section 7.XX related effects which are also involved in the
encounter and separation or CRIPs and SSRIPs discussed earlier. In these cases the separation of cage partners can be assisted (same sign charges), or hindered (opposite charges) depending on the sign and magnitude of Coulombic interactions and the polarity of the solvent molecules. Such effects are usually negligible in energy transfer.

\section*{7.13 Distance-Time Relationships for Diffusion}

How long does it take a molecule in a fluid solution to diffuse a given distance from an initial location? Eq. 7.95 shows the dependence of the diffusion coefficient, $D$, with temperature, size and solvent viscosity.

Diffusion theory predicts that the average displacement $x$ of a diffusing particle during a time $t$ is related to the diffusion coefficient $D$ of the particle according to:

$$x = \sqrt{2Dt}$$  \hspace{1cm} (ee.100)

This simple expression takes into account the complex zig-zag pattern involved in the displacement of a molecule in solution. Figure 7.24 shows the displacement achieved by a small molecule in a non-viscous ($D \sim 10^{-5} \text{ cm}^2/\text{s}$) and a viscous ($D \sim 10^{-10} \text{ cm}^2/\text{s}$) solvent; the latter may represent a polymer system.
Figure 7.24: Graphs of the relationship between diffusional distance and time for a small organic molecule in a fluid (non viscous) and polymer-like (viscous) solvent.

Abuin and Lissi[,,91Abu1] have calculated the mean distances traveled by oxygen in water at room temperature. These data are reproduced in Table 7.4.

**Table 7.4**: Mean distances traveled by an oxygen molecule, in water at room temperature, for different elapsed times. [,91Abu1]

<table>
<thead>
<tr>
<th>Time</th>
<th>$x$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ps</td>
<td>1.6</td>
</tr>
<tr>
<td>1 ns</td>
<td>16</td>
</tr>
<tr>
<td>100 ns</td>
<td>160</td>
</tr>
<tr>
<td>4 µs</td>
<td>$1 \times 10^3$</td>
</tr>
<tr>
<td>1 ms</td>
<td>$1.6 \times 10^4$</td>
</tr>
</tbody>
</table>
The motion of a molecule in solution follows a complex pattern, termed a "random walk", largely determined by its collisions with other molecules, specially those of the solvent. As discussed above, when two molecules such as *D and A "meet" in solution and become partners in a solvent cage to form $D^*A$, we say that an "encounter" has occurred involving the two molecules. When an encounter occurs, the molecule undergoes many collisions until it either reacts or separates. In the context of the previous Section, a diffusion-controlled reaction is one where the probability of reaction between *D and A after an encounter to form $D^*A$ is much larger than the probability of separation to form *D + A. How long does an encounter last? Let us compute the time $t$ from Eq. 7.100, a typical diffusion coefficient ($D$) in a solvent such as benzene at 25°C may be around $2 \times 10^{-5}$ cm$^2$/s; if we assume the encounter to be over when one of the molecules has traveled a distance equivalent to the size of several solvent molecules (e.g. $x \sim 10$ Å, equivalent to about 2 benzene molecules), then we obtain a rough estimate of the time required by applying Eq. 7.100 of about $2.5 \times 10^{-10}$ s. During this time the solute molecules will undergo many collisions. It has been suggested that since even displacements of molecular dimensions are achieved on a complicated zig-zag path (random walk) consisting of a great number of single segments, then Eq. 7.100 can be applied even to such very small displacements.

### 7.14 Diffusion Control in Systems Involving Charged Species

Coulombic attractive and repulsive interactions can play an important role in determining the kinetics with which charged particles encounter or separate. On a first approximation the effects only need to be taken into account when both reactants are charged. That is, cage effects can be controlled in importance and
duration by Coulombic interactions in addition to those features which are charge independent (viscosity, temperature and molecular dimensions).

It is important to realize that in the cases of electron transfer the effect of charge may be quite different on the reactants and on the products. For example, let us assume that a pair of initially uncharged donor and acceptor interact by transferring a single electron form D to A (Eq. 101).

\[
D^* + A \xrightarrow{k_{\text{DIF}}} D^*A \xrightarrow{k_{\text{et}}} D^{+},A^- \xrightarrow{k_{\text{DIF}}^c} D^{+\bullet} + A
\]

In the case of Eq. 7.101, Coulombic effects play no role on the initial encounter of the reactants, but would contribute an attractive interaction between the products $D^{+\bullet}$ and $A^{\bullet-}$, which will then separate more slowly than they would if they had no charge, i.e.:

\[
k_{\text{DIF}}^c < k_{\text{DIF}}
\]

where the superscript "c" indicates charged species. The relationship of Eq. 7.102 is valid when the two products have opposite charges.

A common reaction following photoinduced electron transfer is back electron transfer, for which we use the subscript "bet" in Eq. 7.103. Note that back electron transfer ($k_{\text{bet}}$) generally will regenerates D in its ground state, unless there is an excited state that can be populated between the radical ion pair and the
ground states of D + A. If the encounter is longer lived, then the probability of back electron transfer will increase (Eq. 7.103).

\[
\text{Probability of bet} = \frac{k_{\text{bet}}}{k_{\text{bet}} + k_{\text{DIF}}} \quad (ee.103)
\]

This back electron transfer may result in an inefficient reaction of *D and A, even if the initial electron transfer occurred with very high efficiency.

The diffusion Eq.s given before need to be modified to accommodate the electrostatic forces. The electrostatic potential \(U_{es}\) is given by:

\[
U_{es} = \frac{Z_A Z_B e^2}{4\pi \varepsilon_0 \varepsilon r} \quad (ee.104)
\]

where \(Z_A\) and \(Z_B\) are the charges of the ions involved, \(e\) is the charge of the electron, \(\varepsilon_0\) the permittivity of vacuum, \(\varepsilon\) the dielectric constant of the solvent and \(r\) the separation between the particles of charge \(Z_A\) and \(Z_B\). This potential cancels if either \(Z_A\) or \(Z_B\) are zero.

The rate constants for diffusion of charged particles are obtained by interpretation of the diffusion Eq.s incorporating the potential of Eq. 7.104. While the detailed coverage of this analysis is beyond the scope of this book, it is useful to develop a sense of the magnitude of the corrections to \(k_{\text{DIF}}\) that can be expected. The connection (see Figure 7.25) is a function of the products of the solvent dielectric constant \((\varepsilon)\) and the distance \(\sigma\) (defined as in Eq. 7.94). Note the extremely large corrections in non-polar solvents; not surprisingly, bringing close together two particles with charges of the same sign in a non-polar solvent is very difficult.
Figure 7.25: Dependence of the electrostatic correction term on the product of the charges \((Z_A Z_B)\) and the product of the solvent dielectric constant \((\varepsilon)\) and the distance \((\sigma)\) in Å.

For example, for a critical distance of 3 Å the correction terms in water \((\varepsilon = 80)\), acetonitrile \((\varepsilon = 36)\) and dichloromethane \((\varepsilon = 8.9)\) are 0.25, 0.03 and \(1.6 \times 10^{-8}\) for \(Z_A Z_B = 1\) and 2.6, 5.2 and 21, respectively for \(Z_A Z_B = -1\).

Note that there is a clear distinction between the Coulombic effects just described, which influence the delivery between donor and acceptor, and effects due to solvent reorganization described under Marcus theory, which influence the rate constant \((k_{et})\) of the actual electron transfer step in Eq. 7.101.

7.15 Effect of Rapid Molecular Processes on the Mechanism of Processes Approaching Diffusion Control

Our analysis of diffusional processes in Sections zz - zz was based on the assumption that reactants around a given molecule, for example of A molecules
around *D, (see Eq. 7.93) were randomly distributed. However, there are situations where the distribution of D and A molecules in solution starts out random, but suddenly becomes non-random. This situation can arise when the reaction of interest is so fast compared with rates of transport of products of reaction of *D and A, that as an excited donor molecule *D reacts, it can significantly deplete the concentration of A molecules in its immediate neighborhood. Interestingly, the effect takes place even when *D can react only once.

Again, for the purposes of illustration, we describe these rapid processes in the context of a near diffusion controlled energy transfer reaction as shown in Eqs. 7.105, 7.106 and 7.107.

\[
\begin{align*}
D & \xrightarrow{h\nu} D^* & \text{(ee.105)} \\
D^* & \xrightarrow{k_D} D & \text{(ee.106)} \\
D^* + A & \xrightarrow{k_{ET}} D + A^* & \text{(ee.107)}
\end{align*}
\]

Depending on the values of \(k_D\) and the diffusion parameters that determine \(k_{ET}\), quenching of *D by A can occur in three distinct regimes:

(a) **Quenching controlled by diffusional processes.** This is the most common regime and corresponds to the examples we have already discussed in **Section XX**. We normally encounter this situation when processes occur in long time scales, or when quenching is significantly slower than diffusion control. In fluid solvents it is normally the only quenching regime we need to be concerned with when the lifetime of
*D under the conditions of the measurement exceeds $10^{-8}$ s because with such a long lifetime separation of the reactive partners will be a certainty in fluid solutions.

(b) **Quenching influenced by “transient effects”**. The term “transient” refers to rapid quenching events that lead to a time-dependent rate constant. This situation can become quite important when concentrations are high and lifetimes are short, leading to a condition where redistribution of quenchers (A) around a probe molecule (*D) cannot be re-established during the lifetime of *D. In fluid systems these effects will be common when lifetimes are near or less than $10^{-8}$ s and the quenching rate constants exceed 20% of the rate constant for diffusion-controlled processes (i.e. $k_{OBS} \geq 0.2 k_{DIF}$).

(c) **Static quenching**. Occurs when quenching does not require actual transport of molecules through the solution. These processes are characteristic of systems where diffusion is inhibited, such as in the case of solid matrices. They are generally unimportant in fluid solution unless relatively stable complexes of D and A are preformed or if the separation of D and A is fixed by covalent spacer. We will discuss one example of this case (The Perrin Formulation) later in this chapter.

The influence of transient effects (where normal diffusion Eq.s break down) on quenching processes in solution corresponds to case (b) above. As our experimental techniques have enabled the measurements of faster and faster processes, the examples where these types of effects have become of increasing importance will become increasingly common. Today our ability to study fast
reactions can access processes occurring in the tens of femtoseconds (1 fs = 10^{-15} s). For example, if we employ Eq. 7.100, or Figure 7.24 to calculate the average path traveled by a molecule with D ∼ 10^{-5} cm^2 s^{-1} in 100 fs, 10 ps and 1 ns, we find these distances to be 0.14 Å, 1.4 Å and 14 Å, respectively, clearly, in at least the first two cases, distances that are too short for diffusion to be able to re-establish a random equilibrium distribution of molecules if the equilibrium was suddenly perturbed.

Let us assume that a solution contains D and A distributed completely at random, the way they would be if the other type of molecule were not present. Noyes[61Noy] has reported an elegant treatment of diffusional processes in these systems. We now excite D into *D; those molecules of *D that have nearby A neighbors can be expected to react sooner than those having distant A neighbors. After a short time, if we examine the distribution of A molecules around surviving *D molecules, we will find the concentration of A molecules lower than in the bulk of the solution. Naturally this reflects the fact that those A molecules that were initially near *D molecules have already led to the deactivation of *D. This generates a concentration gradient around surviving *D molecules that is directly related to the existence of the reaction between *D and A. Figure 7.26 illustrates qualitatively the role of these effects for a very fast reaction, for example, one that occurs during every encounter.
Figure 7.26: Transient effects on excited state quenching. At the shortest times all four donors are excited. In the middle column, B, who had a nearest neighbor has been quenched, while on the right B and S have been quenched. The survivors, A and C no longer have random distribution around them. On average quenchers are further away then at t = 0. Formally the rate of quenching appears to be faster at the shortest times.
The same effect can be shown on the concentration of quenchers that surround a given molecule at different times, i.e., Figure 7.27.

\[
\text{Note that in all cases the concentration of A for distances less than } \sigma \text{ is zero. This reflects that molecules of A and D cannot approach closer than the sum of their radii (cannot interpenetrate). The initial situation (a) is one where, except for the limitation relating to } \sigma, \text{ the concentration of A molecules is the same everywhere, regardless of their possible proximity to molecules of D. Following excitation the } ^*D \text{ molecules with nearby A neighbors react rapidly, causing a partial depletion (Figure 7.27b); for example a typical time for this type of behavior to occur may be } 10^{-9} \text{ s. After some time we reach a situation where the concentration of A around remaining excited molecules (} ^*D \text{) is determined by the diffusion of A from the bulk towards the vicinity of } ^*D. \text{ At a distance } \sigma \text{ the concentration remains zero because molecules react as soon as they reach this position. Once this condition has been reached, the observable rate constant will correspond to } k_{\text{DIF}} \text{ as defined earlier (see Eq.s 7.93 and 7.96). It follows from the}
\]

**Figure 7.27:** Evolution of the concentration of A molecules around excited donors, *D, following excitation of D under conditions where transient terms are of importance. Note that \( \sigma = r_A + r_D \), following Eq. 94.
above discussion that we would expect rates of quenching at short time scales to be faster than those in the diffusional regime.

### 7.16 Energy Transfer in the Absence of Diffusion

It has been experimentally observed that energy and electron transfer can occur even in rigid systems. We can inquire about possible mechanisms for the material transport *delivery* of electronic excitation energy or of an electron from a donor \( \text{D} \) to an acceptor \( \text{A} \). *Possible* mechanisms may include:

(a) **Physical mass transport**: i.e. the system although macroscopically rigid is not really rigid at the molecular level.

(b) **Proximity**: The system is rigid, but donors and acceptors are sufficiently close to permit transfer. This situation applies to preformed complexes of \( \text{D} \) and \( \text{A} \) for molecules for which a covalent spacer separated \( \text{D} \) and \( \text{A} \). It is also common that in rigid systems processes competing with energy or electron transfer are slower than in solution and therefore the time scale available for successful transfer is much longer than in fluid media.

(c) **Conducting media**: The material that provides the rigid environment assists in the transfer process.

(d) **Energy or electron migration**: The molecules we are dealing with have a mechanism by which they can effectively become *molecular wires*.

We note that cases (a) and (c) relate to properties of the matrix, which perhaps can be tested with other D-A pairs. If we can eliminate these two cases
from our list, then, our plausible mechanisms become proximity (b) and migration (d).

Migration mechanisms are most likely to occur in organized systems (see Chapter xx) or in polymeric materials. For example, it is well established that in polymers made of naphthalene units containing a few anthracene units (frequently) as end groups,[Guillet, 1985 #17; Holden, 1981 #18; Holden, 1980 #19] fluorescence emission occurs predominantly from the anthracene groups. The effect is largely due to the hopping of the energy among naphthalene units until the energy is located next to an anthracene group, in which case its lower excited state energy provides an effective trap for the energy, see Figure 7.29. The effect is called antenna effect; naturally 'hops' take place in both directions, only the successful ones being shown in Figure 7.29. The distance traveled in a one dimensional system is proportional to $\sqrt{\text{time}}$ (Eq. 7.100).

**Figure 7.29:** Schematic representation of the antenna effect in a polymeric system showing energy hopping to a trap at the end of the chain.
Similarly, in photosynthesis the majority of the chlorophyll molecules are photochemically inert, but they function as an antenna delivering the energy to the reaction centers. Effects of aggregation on photoreactions are discussed in Chapter zz.

While mechanisms (b) and (d) may be plausible, if we are dealing with small molecules (as opposed to polymers) which show no tendency for self-aggregation, the most probable mechanism is probably (b): i.e. energy or electron transfer results from proximity. Here the term 'proximity' is used to refer to an ensemble of pairs of molecules, all or some of which are closer than some critical distance required for transfer to occur. The Perrin Formulation of quenching of *D by A is presented in the next Section is the simplest model that allows the interpretation of data in systems of this type.

**The Perrin Formulation of Quenching. The Quenching Sphere.**

We defined earlier three regimes for quenching, i.e. determined by diffusional processes, influenced by transient effects, and finally, static quenching. The first two require transport of molecules through the medium, and are therefore influenced by the values of the diffusion coefficients. The third one, static quenching, does not require molecular motion because *D and A are within a “quenching sphere”. In most cases this will mean that we are dealing with a rigid system (crystals, glass, polymer matrix) where mobility may be severely restricted; however, static quenching may also involve systems which are usually viewed as incorporating mobile molecules, provided the time scale for quenching is sufficiently short that molecular motion is not significantly in the times involved. However, in liquids if D and A are complexed (D---A)the
excitation of D to a *D---A complex (an exciplex) which can undergo a quenching process before separation of *D and A into freely diffusing species occurs.

The Stern-Volmer formulation employed earlier in this chapter is not valid under conditions of static quenching. The Perrin Formulation (Eq. 7.118 below) is a very simple model which assumes that an effective "quenching sphere" exists about *D, which may be used to analyze the experimental data in such situations.

The Perrin model (Figure 7.30) assumes:

(a) There exists a volume in space - or more precisely a "quenching sphere" - about *D whose radius is R and if a quencher molecule, A, is within this quenching sphere, then *D is deactivated with unit efficiency.

(b) *D and A cannot undergo displacements in space which remove it from the "quenching sphere" during the lifetime of *D.

(c) If an A molecule is outside of the quenching sphere, it does not quench *D at all.

The situation is outlined in Figure 7.30. The assumptions of the Perrin model are equivalent to defining a "sphere of effective quenching", of radius R. If this sphere contains one or more quencher molecules the excited molecule is quenched with 100% efficiency (case a in Figure 7.30). On the other hand, if the quencher is located outside the quenching sphere, (case b in Figure 7.30), no quenching of the excited molecule occurs.
The efficiency of quenching is given by:

$$\ln \left( \frac{\phi^o}{\phi} \right) = V N_A [A] \quad (7.108)$$
where $\phi^0$ and $\phi$ are the efficiencies (usually quantum yields for fluorescent systems) for donor emission in the absence and presence of quencher, respectively, $V$ is the volume of the active sphere of quenching (in cm$^3$)$^\dagger$, $N_A$ is Avogadro’s number, and [A] the concentration of quencher in units of M. A plot of $\ln (\phi^0 / \phi)$ vs. [A] yields $N_A V$ and given $N_A$, $V$ can be determined. In spite of its remarkable simplicity, the model works well for many cases of energy and electron transfer. Some examples will be presented later.

In general, we prefer to relate to the radius of the quenching sphere, rather than its volume, i.e.:

$$R = \left( \frac{3V}{4\pi} \right)^{1/3}$$  \hspace{1cm} (ee.109)

The radius $R$ is also directly related to the concentration of [A]. If appropriate conversion factors for the units are introduced the relationship is:

$$R \text{ (in Å) } = 6.5 [A]^{1/3}$$ \hspace{1cm} (7.110)

(with [A] in M units)

These distances work out to 6.5 Å for a 1M solution and 30.2Å for 0.01M. Quite clearly, for concentration below $10^{-2}$ M the molecules are on the average quite far apart.

The Perrin model has been successfully applied to both energy and electron transfer. In the latter case Miller et al. [Miller, 1982 #4] have shown that electron transfer can occur at long distances. In one example to be illustrated

$\dagger$ This is analogous to the division by 1000 used earlier in equation ee.93.
later R was 17 Å and 25 Å for electron transfer by the singlet and triplet states, respectively.

The Perrin model predicts that the lifetime of *D should not be affected by the presence of the energy or electron acceptor A. That is, molecules within the quenching sphere will be quenched, but those outside the sphere should have no effect on *D, such that "surviving" donors will decay with the same lifetime as in the absence of A. While this prediction is not accurate and the lifetimes do show a fall off with increasing quencher concentration, the predictions work well for the modeling of steady state quenching data.

References