Delivery

Need and mechanism for energy or electron delivery

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

(2) **Diffusional processes**. 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**. 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.

Role of Molecular Diffusion

free diffusing molecules → *one encounter* → *many collisions* → *one favorable collision leads to successful transfer*

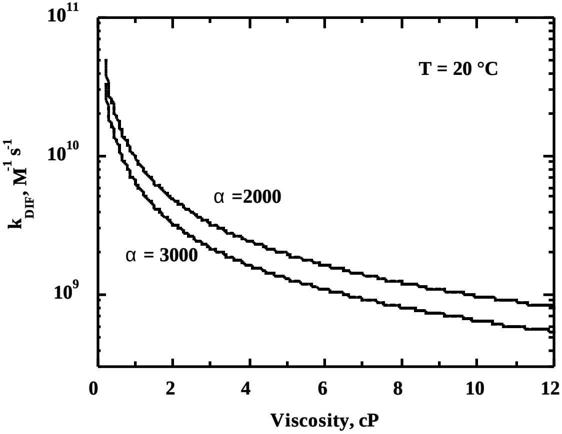
$$k_{\mathrm{DIF}} = 4\,p\;N_A \sigma \mathbf{D} \times 10^{-3}$$

$$\sigma = r_A + r_D$$

$$\mathbf{D}_A = \frac{kT}{6\,\pi\eta r_A}$$

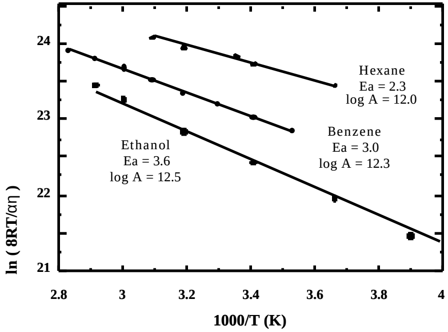
$$k_{\mathrm{DIF}} = \frac{8RT}{\alpha\eta} \qquad (\alpha = 3000)$$

Diffusional rate constants calculated with Debye's equation



Calculated values of k_{DIF} based on Debye's equation for a range of common viscosities.

Temperature dependence of diffusion



Temperature dependence of the diffusional rate constants calculated with equation (α = 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

(a) The measured value of the experimental bimolecular rate constant, k_{OBS}, is close to that calculated with Debye's equation

(b) The experimental value of k_{OBS} is a function of T/η, as expected

(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.

Mean distances traveled by an oxygen molecule, in water at room temperature, for different elapsed times.

Time	***x* (Å)**
1 ns	16
100 ns	160
4 μs	1×10^3
1 ms	1.6×10^4

Exothermic energy transfer

The rate constants for energy transfer processes which are exothermic by more than 3-4 kcal/mol and are spin allowed, frequently approach the diffusion controlled limit.

$$k_{diff} = \frac{8RT}{2000\eta} \qquad 2 \times 10^{5}\,\frac{T}{\eta}$$

Representative diffusion controlled rate constants in units of: 10^{10} M^{-1} s^{-1}	
isopentane	4.6
benzene	1.6
water	1.1

Example of Near Diffusion-Controlled Reactions

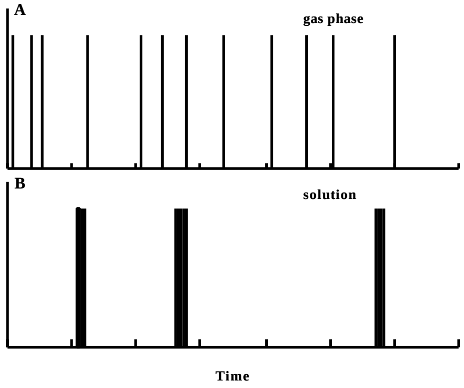
$$D^* \longrightarrow D$$

$$D^* + A \underset{k_{-DIF}}{\overset{k_{DIF}}{\rightleftharpoons}} \overline{D^*A} \xrightarrow{k_{ET}} \overline{DA^*} \xrightarrow{k_{-DIF}} D + A^*$$

$$k_{OBS} = \frac{k_{DIF}\, k_{ET}}{k_{-DIF} + k_{ET}}$$

The cage effect

When two molecules meet and collide in solution, they find themselves in a "crowded environment" that tends to push them together many times before they succeed in separating



Energy Transfer in the Absence of Diffusion

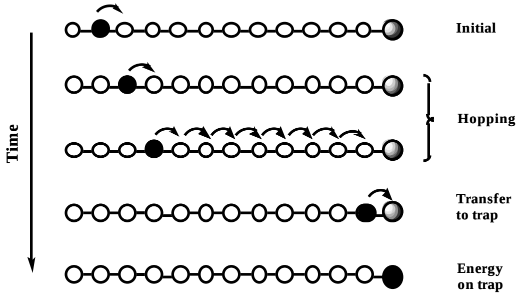
(a) Physical mass transport: i.e. the system although macroscopically rigid is not really rigid at the molecular level.

(b) Proximity: The system is rigid, but donors and acceptors are sufficiently close to permit transfer. 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.

Antenna effect in a polymeric system showing energy hopping to a trap at the end of the chain



	Ground state	Excited
Main group	○	●
Trap group	◍	⬤

The Perrin Formulation

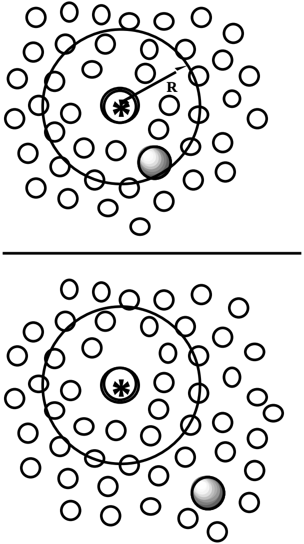
The Perrin model assumes:

(a) The donor and acceptor cannot undergo displacements in space during the lifetime of D*.

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

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

The Perrin model



(a)

$\varphi = 0$

⊛ **= D***

● **= A**

○ **solvent**

(b)

$\varphi = 1$

$$\ln(\varphi^\circ/\varphi) = V N_A [A]$$