

FEATURE ARTICLE

Medium Effects on Elementary Charge Transfer Processes in Liquid and Solid Environments

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Received: November 5, 1996[®]

A systematic discussion of the effect of the medium on the elementary act of electron and proton transfer reactions is given. The effects due to the softening or freezing of different discrete or continuum vibrational modes are elucidated. The role of dielectric polarizability of the environment and its spatial dispersion and the influence of the ionic atmosphere are discussed for different reaction types. The options offered by biological macromolecules as the reaction medium are considered. Focus is put on the differences of reaction rates in liquids and solids with an emphasis on some counterintuitive effects, which follow from the detailed analysis.

Introduction

Chemical reactions involving charge transfer steps between the reactants in homogeneous or electrochemical systems are of importance both for the understanding of fundamentals of chemical kinetics and in respect to numerous applications. Electron and proton transfer represent the most ubiquitous reactions of this kind. They constitute the fundamental reaction steps in homogeneous acid/base catalysis, in homogeneous and electrochemical redox reactions including hydrogen and oxygen evolution, in processes in fuel cells, etc.

Historically, the development of the theory of charge transfer began for solids where multiphonon electron transitions between localized states were discovered.^{1–3} These included both electron-hopping mobility in polar crystals and light absorption and radiationless processes in impurity centers. The theory was later extended to the crystal defect mobility.^{4,5} Theoretical views on *chemical* charge transfer (focused on the reactions in electrolyte solutions, both in the bulk and at electrode surfaces), rooted in similar or closely related concepts and formalism, began to appear in the 1950's, with tremendous impact on all later work in this broad area of chemistry.^{6–10} In recent years the interest in reactions in the solid phase has increased. This is prompted by the need for a new theory of the microscopic processes behind the operation of a variety of solid state electrochemical devices (involving, for example, the metal/solid electrolyte interface).¹¹ This also extends to exciting new systems involving organized molecular ensembles (such as thin films, conducting polymers, adsorbed layers, molecular clusters, and biological macromolecules),¹² which offer many new perspectives both in basic studies and in applications. Two different main phase states (liquid and solid) in which the reactions proceed are available. In addition, organized molecular ensembles in a broad sense constitute a phase environment "intermediate" in nature between the other two. The central

two questions now arise; what are the main differences between these systems? and which of the media is the "better" for the reaction?

The aim of this article is to approach an answer to these questions and to address the factors which affect the reaction rate in condensed phases. Focus is on differences between the liquid and solid environment, and special attention will be given to "counterintuitive" effects, which emerge from the detailed quantum mechanical theory.

Depending on the complexity of reactions, the overall mechanism may involve different consecutive and/or parallel steps. The system of kinetic equations, which describe these processes, reflects the balance between the different steps through chemical transformations and transport fluxes. The latter are treated by Smoluchowski terms (diffusion and migration), while the former are determined by "source" and "sink" terms proportional to the concentrations of reactants and rate constants of the elementary acts.¹³

The overall reaction mechanism involves at least two major groups of steps: (i) the transport of the reactants and reaction products to and from the reaction zone and (ii) the elementary reaction act itself converting the reactants to products. Either may in principle be rate determining. If the transport stage is the slowest one, the problem reduces to the solution of pure transport equations. On the other hand, if the rates of given elementary processes, which are consequent to the transport stage, are the slowest, the overall reaction rate will be determined by the quasi-equilibrium reactant concentrations and the rate constants of the elementary act.

In the absence of convection the transport in liquids is due to molecular diffusion. The diffusion coefficients for ions and molecules in liquids are about 10^{-5} cm²/s. At a diffusion length $\sim 10^{-6}$ cm a flux equivalent to the rate constant of electrochemical processes $k \sim 10$ cm/s may be provided. Diffusion is slower in systems where the liquid phase is confined in the pores of a solid matrix since the same thickness of the material layer here corresponds to longer diffusion lengths.¹⁴ Diffusion coefficients for atomic species in common solids are much smaller than in liquids,¹⁵ the difference reaching several orders of magnitude.

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[®] Abstract published in *Advance ACS Abstracts*, June 15, 1997.

However, the mobility in some materials is considerably faster. This applies, for example, to the proton motion in fast proton conductors.¹⁶ Diffusion along the grain boundaries and interfaces, as well as in the channel structures, may also be much faster than in the bulk of ordinary crystals. Solid electrolytes represent a class of solids with ion mobility approaching that in liquids.^{17,18} For example, the diffusion coefficient of Ag⁺ ions in Rb₄AgI₅ solid electrolyte exceeds 10⁻⁶ cm²/s. An appropriate choice of the solid material may thus considerably relax the transport limitations for the reaction and approach the limit in liquids. Since these differences are not principal ones, we shall primarily discuss the elementary act of reaction.

General Expressions for the Charge Transfer Rate Constant

The probability of elementary thermally activated charge transfer in a condensed medium at fixed distance R between the reacting species or between the reactant and the electrode surface has the form^{10,19}

$$W(R) = \frac{\omega_{\text{eff}}}{2\pi} \kappa_e e^{-(F_a/k_B T)} \quad (1)$$

where ω_{eff} is the effective frequency for motion along the atomic coordinates, κ_e the transmission coefficient, and F_a the activation Gibbs free energy. The rate constant is obtained by averaging $W(R)$ over the distance R

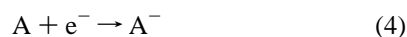
$$k = \langle W(R) \rangle = \int dR \Phi(R) W(R) \approx \Phi(R^*) W(R^*) \Delta R \quad (2)$$

where $\Phi(R)$ is the distribution function for the reactants, R^* the distance for optimal rate, and ΔR the width of the reaction zone. $\Phi(R)$ is the probability of approach of reactants to the reaction distance. For bulk processes, it is given by the reactants' binary correlation function. For reactions at surfaces, $\Phi(R)$ is the reactants density distribution near the surface. $\Phi(R)$ depends on short-range forces and electrostatic interaction between the reactants. When the positions of the reactants are fixed by the structure of the solid or in a macromolecule the meaning of $\Phi(R)$ is different. $\Phi(R)$ then determines the probability of realization of such a structure, or the number of reaction pairs.

If the reactants are similarly charged, the character of the dielectric response of the medium and Debye screening by the electrolyte are the most important determinants for $\Phi(R)$. The larger the dielectric constant and the higher the ion concentration, the weaker is then the electrostatic repulsion. This dominates over corresponding electrostatic effects in $W(R)$, leading to an increase of the rate constant. On the other hand, if one of the reactants is neutral or the reactants are charged oppositely, the reaction distance is determined by the competition between the decrease of the electronic matrix element and the short-range repulsion. The rate constant is then largely determined by $W(R)$ itself. Unless otherwise stated, the properties of $W(R)$ will be the main subject of this article.

Representative Charge Transfer Reaction Classes

Simple Reactions in the Bulk and at Two-Phase Boundaries. Electron and proton transfer are the fundamental constituents of electrochemical reactions. The former consists in the exchange of an electron between the electrode and a reactant



where A represents ionic or molecular species. Particular examples are reactions involving a wealth of transition metal complexes, such as [Fe(H₂O)₆]^{2+/3+}, [Fe(CN)₆]^{3-/4-} etc., small molecules such as O₂, or the products of their dissociation on the surface (e.g., adsorbed O-atoms).

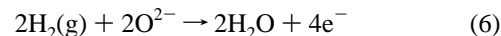
The reactions 3 and 4 may lead either to an increase or a decrease of the charge of the reacting species. In electrochemical proton transfer the adsorption or desorption at the electrode surface thus occurs along with electron transfer



The behavior of the proton in the reaction is, moreover, usually of quantum mechanical nature and resembles that of the electron,^{10,20-25} but is more sensitive to the details of the interaction with the environment.

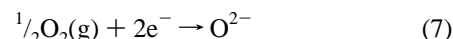
A variety of charge transfer processes between two reactants (i.e., redox electron transfer reactions between metal complexes, proton transfer in acid base catalysis, dissociative electron transfer, etc.^{10,26}) take place in the bulk. Charge transfer reactions, both at electrodes and in the bulk, may proceed also in solid environments. Examples here are electron transfer in mixed valence compounds in solid matrices,²⁷ proton transfer in clathrates,²⁸ and metal deposition from solid electrolytes.²⁹

Reactions at Three-Phase Boundaries. Special attention has been given to reactions at three-phase boundaries such as gas–electrolyte–metal systems, important in fuel cells.³⁰ In high-temperature solid oxide fuel cells the following processes are central. The anode is a composite ceramic material, consisting of the grains of the metal catalyst and solid electrolyte and of pores. The molecules of the H₂ gas, penetrating into the pores, adsorb on the catalyst surfaces and dissociate into two adsorbed H-atoms, which then take part in the reaction



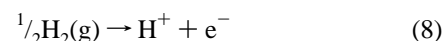
Possible mechanisms of this reaction are discussed in the literature.³¹ For example, upon dissociative adsorption of H₂, one atom transfers its electron to the metal and forms a chemical bond with an O²⁻ ion of the electrolyte at the three-phase boundary. The OH⁻ ion recombines with another H⁺ to form a water molecule.

The cathode is a porous mixed ionic and electronic conductor (perovskite), in which the gaseous oxygen dissociates at the two-phase boundary. Each oxygen atom accepts two electrons from the electrode and diffuses into the electrode in the ionic form

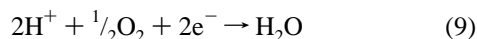


Reaction 6 is composed of electron transfer between the adsorbate and the metal and proton transfer to the O²⁻ at the surface of the electrolyte. Due to the essentially heterogeneous, three-phase environment for the reaction, these processes cannot be directly mapped on the existing theory developed in the context of more conventional electrochemical reactions at the contact between two phases. However, the processes do possess a number of features in common with processes in the bulk or at the two-phase boundaries, which are considered in this article.

Reactions in low-temperature fuel cells³⁰ with proton-conducting polymer membranes are closer to these processes. The reaction



proceeds at the anode by proton transport from the adsorbed state into the polymer electrolyte. At the cathode, the reaction



involves proton transfer from the polymer electrolyte to the adsorbed oxygen. Both reactions take place at three-phase boundaries (catalyst–gas–electrolyte), and in this sense they are different from conventional two-phase reactions. They exhibit, however, explicitly the central proton transfer step in the condensed medium. The relatively low operating temperatures can, furthermore, make the elementary rate limitations more important.

Charge Transfer in Biological Systems. Electron and proton transfer are also the central elementary reactions in biological processes, most conspicuously in the electron transport chains of photosynthesis and respiration, and in hydrolytic and redox enzyme processes. Biological elementary processes follow of course the same fundamental physical principles as charge transfer in less glamorous physical and chemical systems. The three-dimensional structure of the molecules, metalloproteins and nucleic acids in particular, and their supramolecular organization in protein and membrane complexes, however, endow biological charge transfer with special features. These are distinctive for this category compared with similar processes where only small, freely mobile molecules are involved. The features in particular, are (a) “long-range” electron transfer, which occur over distances which significantly exceed the structural extension of the donor and acceptor groups. Fast electron transfer is still feasible since these processes frequently involve laser or pulse radiolysis generated radicals with small nuclear activation due to a large driving force. This can apply both to the individual molecules, say metalloproteins,^{32–38} and to the spatial organization of the donor and acceptor in large membrane-spanning protein complexes such as cytochrome oxidases^{39–41} or the photosynthetic reaction centers.^{42,43}

(b) The electronic and molecular structure of the intermediate protein material and the structural organization in facile long-range electron transfer routes, which involve favorable electronic coupling along peptide backbones and hydrogen bonds.

(c) Cooperativity between several metal centers, examples of which are the cooperation between the heme groups in the oxygenation equilibria of hemoglobin,⁴⁴ or the multielectron transfer patterns of the four-heme cytochrome *c*₃ proteins.^{45,46} Cooperativity is transmitted through the protein conformational dynamics and poise the protein for facile transfer of more than a single particle, be it a dioxygen molecule, an electron, or a proton.

(d) Particular surface structural elements of the biological macromolecules, which are elements that can be geometrical structural features such as in many enzymes, or localized charge accumulation as in the plant plastocyanins or other electron transfer proteins. Molecular recognition features can be linked with protein dynamics in the sense that the recognition event is accompanied by conformational changes leading to suitable docking of the reacting molecules (for different views on this, see refs 47–51).

Protein and membrane charge transfer is thus endowed with special features of individual and supramolecular organization, rooted in the three-dimensional structure and in the hierarchy of molecular and collective relaxation times. These extend over many orders of magnitude and impose intriguing roles of the protein and membrane matrices which at the same time are parts of the reacting molecular entities and constitute the environmental reaction medium. For these reasons biological charge transfer are also interesting models to be emulated in molecular

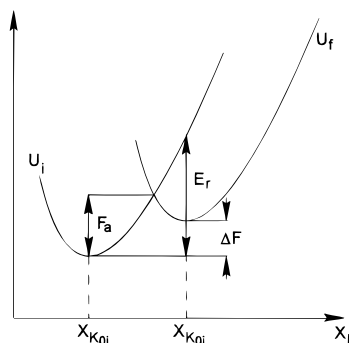


Figure 1. Diabatic free energy surfaces. F_a is the activation Gibbs free energy, ΔF the Gibbs free energy of transition, E_r the reorganization energy.

electronic devices and other synthetic long-range, directional charge transfer systems.

The Role of the Medium in the Elementary Act Dynamics: Simple View

The transition from the initial to the final state is usually described in terms of motion on the potential energy or Gibbs free energy surfaces (diabatic U_i and U_f or adiabatic U_0 and U_{ex} , depending on the character of the transition).^{10,22} The diabatic free energy surfaces represent the Gibbs free energy of the reacting complex in the initial or final states as a function of the vibrational or translational coordinates of the reactive modes. In order to show how the surface parameters affect the activation barrier, we consider a simple electron transfer reaction in the framework of the simplest formalism.

The reactive modes are the ones which interact with the electron. The interaction V_{ev} is different when the electron is localized at the donor or the acceptor and adds to the Gibbs free energy of the vibrational modes thus forming two different free energy surfaces

$$U_i = U_0 + V_{ev}^i \quad (10)$$

$$U_f = U_0 + V_{ev}^f \quad (11)$$

Vibrational modes can often be represented as a set of harmonic oscillators with the normal coordinates x_k and vibrational frequencies ω_k . The interaction of the electron with the vibrational modes can often be considered as linear in x_k . We therefore have for the free energy surfaces

$$U_i = \frac{1}{2} \sum_k m_k \omega_k^2 x_k^2 - \sum_k \gamma_{ki} x_k + \epsilon_{oi}$$

$$U_f = \frac{1}{2} \sum_k m_k \omega_k^2 x_k^2 - \sum_k \gamma_{kf} x_k + \epsilon_{of} \quad (12)$$

where γ_{ki} and γ_{kf} are coupling constants, while ϵ_{oi} and ϵ_{of} are the electron energies in the absence of the interaction. Introducing the equilibrium values of the normal coordinates

$$x_{k0i} = \frac{\gamma_{ki}}{m\omega_k^2}$$

$$x_{k0f} = \frac{\gamma_{kf}}{m\omega_k^2} \quad (13)$$

we can transform eqs 12 as (cf. Figure 1)

$$U_i = \frac{1}{2} \sum_k m_k \omega_k^2 (x_k - x_{k0i})^2 + \epsilon_{oi} - \frac{1}{2} \sum_k \frac{\gamma_{ki}^2}{m_k \omega_k^2}$$

$$U_f = \frac{1}{2} \sum_k m_k \omega_k^2 (x_k - x_{k0f})^2 + \epsilon_{of} - \frac{1}{2} \sum_k \frac{\gamma_{kf}^2}{m_k \omega_k^2} \quad (12)$$

Equation 14 shows that the reaction free energy is

$$\Delta F = F_f - F_i = \epsilon_{of} - \frac{1}{2} \sum_k \frac{\gamma_{kf}^2}{m_k \omega_k^2} - \epsilon_{oi} + \frac{1}{2} \sum_k \frac{\gamma_{ki}^2}{m_k \omega_k^2} \quad (15)$$

All kinetic parameters involved in eq 1 may be calculated for free energy surfaces of this type. The activation Gibbs free energy F_a is described by the well-known equation⁶

$$F_a = \frac{(E_r + \Delta F)^2}{4E_r} \quad (16)$$

where E_r is the reorganization free energy of the reactive modes

$$E_r = \frac{1}{2} \sum_k m_k \omega_k^2 (x_{k0i} - x_{k0f})^2 = \frac{1}{2} \sum_k \frac{(\gamma_{ki} - \gamma_{kf})^2}{m_k \omega_k^2} \quad (17)$$

(see eq 13). The preexponential factor in eq 1 (denoted below as A) is different for diabatic and adiabatic reactions. It is independent of the vibrational properties of the reactive modes for diabatic reactions^{7,10,52}

$$A_{\text{nonad}} = V^2 \sqrt{\frac{\pi}{\hbar^2 k_B T E_r}} \quad (18)$$

where the electronic matrix element V (or electronic exchange factor) couples the donor and acceptor states. For adiabatic reactions it is equal to

$$A_{\text{ad}} = \omega_{\text{eff}} / 2\pi \quad (19)$$

where the effective frequency ω_{eff} is determined by the vibrational and relaxation characteristics of the reactive modes (see below).

Symmetric Reactions. We consider first the simplest case where the electron is transferred between two identical sites of the lattice or species in the medium (i.e., symmetric or thermoneutral processes as $A^- + A \rightarrow A + A^-$). The transition free energy ΔF is then zero and the activation free energy

$$F_a = \frac{E_r}{4} = \frac{1}{8} \sum_k \frac{(\gamma_{ki} - \gamma_{kf})^2}{m_k \omega_k^2} \quad (20)$$

Equation 20 shows that the activation free energy decreases with the increase of the vibrational frequencies of the reactive modes. *Therefore, the more rigid the structure of the molecular environment of the reaction complex the larger is the reaction rate constant in the case of the nonadiabatic reaction.* This counterintuitive conclusion is equally valid both for the discrete reactive modes and for the dielectric continuum of the medium.

For the latter the reorganization energy is determined by⁶

$$E_r = \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \frac{1}{8\pi} \int d^3 r (\vec{D}_i - \vec{D}_f)^2 \quad (21)$$

where ϵ_∞ and ϵ_0 are the optical (high-frequency) and static (low-frequency) dielectric constants of the medium, while \vec{D}_i and \vec{D}_f are the electric inductions due to the reactants in the initial and final states.

Equation 21 shows that the less polar the medium (i.e., the smaller its static dielectric constant), the smaller is the reorganization energy.⁵³ It is expected that when moving from a liquid to a solid we switch to a more rigid structure around the reactants which is particularly reflected in lower dielectric constants for ordinary crystals. In the absence of transport limitations, the thermoneutral reactions thus proceed faster in the solid than in the liquid phase. This result is transparent. If the deformation of the crystal lattice did not occur and the fluctuations were entirely frozen, the process would proceed in a resonant tunneling mode. Any displacements of the equilibrium positions of the atoms and fluctuations destroy the resonant configuration.

Nonsymmetric Reactions. The situation is less unambiguous when the electron is transferred between different reactants, in particular at the interface. The activation free energy depends in this case both on the reorganization free energy and the reaction free energy (eq 16); at small ΔF ($\Delta F \ll E_r$)

$$F_a \approx \frac{E_r}{4} + \frac{\Delta F}{2} \quad (22)$$

With the use of eqs 15 and 17 we obtain

$$F_a = \frac{1}{8} \sum_k \frac{(\gamma_{ki} - \gamma_{kf})^2}{m_k \omega_k^2} + \frac{1}{2} \epsilon_{of} - \frac{1}{4} \sum_k \frac{\gamma_{kf}^2}{m_k \omega_k^2} - \frac{1}{2} \epsilon_{oi} + \frac{1}{4} \sum_k \frac{\gamma_{ki}^2}{m_k \omega_k^2} \quad (23)$$

The analogous expression in the continuum approximation has the form

$$F_a = \frac{1}{4} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \frac{1}{8\pi} \int d^3 r (\vec{D}_i - \vec{D}_f)^2 + \frac{1}{2} \epsilon_{of} - \frac{1}{2} \epsilon_{oi} + \frac{1}{2} \left(1 - \frac{1}{\epsilon_0} \right) \frac{1}{8\pi} \int d^3 r D_i^2 - \frac{1}{2} \left(1 - \frac{1}{\epsilon_0} \right) \frac{1}{8\pi} \int d^3 r D_f^2 \quad (24)$$

Equations 23 and 24 show that the effect of the medium now depends on the type of reaction. If, for example, the product molecule becomes neutral after electron transfer to the electrode (see eq 3), or in charge recombination such as in the reaction



the electric induction of the final state vanishes and eq 24 reads

$$F_a = \frac{1}{4} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \frac{1}{8\pi} \int d^3 r D_i^2 + \frac{1}{2} \epsilon_{of} - \frac{1}{2} \epsilon_{oi} + \frac{1}{2} \left(1 - \frac{1}{\epsilon_0} \right) \frac{1}{8\pi} \int d^3 r D_i^2 \quad (26)$$

The activation free energy thus decreases with the decrease of the dielectric constant ϵ_0 . In this case both the reorganization free energy and the free energy of the transition are lowered when the dielectric constant is decreased (Figure 2a).

The situation may be opposite if a neutral molecule becomes charged after the electron transfer from the electrode (eq 4), or, for example, as in the reaction

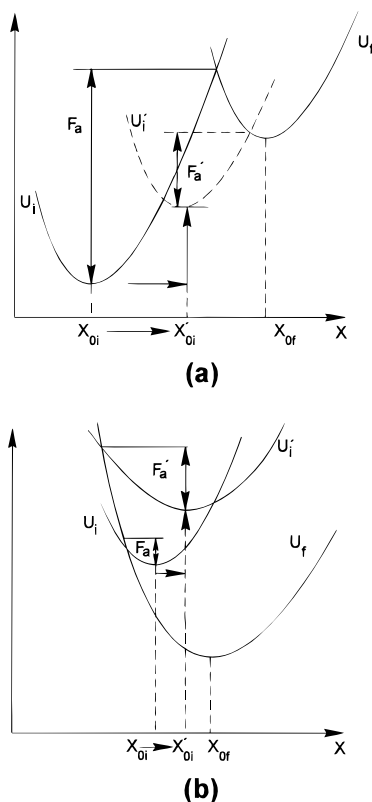
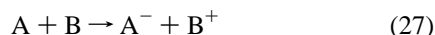


Figure 2. Shift of the Gibbs free energy surface of the initial state ($U_i \rightarrow U_i'$) with the decrease of the static dielectric constant for the reaction of charge recombination, eq 25: (a) normal region, (b) inverted region.



The electric induction of the initial state is then zero, and eq 24 is reduced to

$$F_a = \frac{1}{4} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \frac{1}{8\pi\epsilon_0} \int d^3r D_f^2 + \frac{1}{2} \epsilon_{0f} - \frac{1}{2} \epsilon_{0i} - \frac{1}{2} \left(1 - \frac{1}{\epsilon_0} \right) \frac{1}{8\pi\epsilon_0} \int d^3r D_f^2 \quad (28)$$

The activation Gibbs free energy therefore increases with decreasing dielectric constant. Indeed, the creation of charged species in a less polar medium is less favorable from a thermodynamic point of view, and according to eq 28, this effect dominates over the decrease of the reorganization free energy (Figure 3a).

Nontrivial effects of the medium polarity may be expected for bulk reactions in the so-called “inverted region”.^{54–57} Indeed, eqs 26 and 28 are valid only in the normal reaction region. When the reaction free energy approaches the reorganization energy the full equation for the activation barrier (eq 16) must be used. The inverted region is then eventually reached with decreasing dielectric constant (Figures 2b and 3b). This occurs differently for charge recombination (eq 25) and separation (eq 27).

Consider reaction 27 in the moderate exothermic regime (Figure 3a). The decrease of the medium polarity may change the configuration of the free energy surfaces closer to the thermoneutral situation and then, according to estimates shown in Figure 4, move this configuration to inverted region. As a result, the activation free energy increases. Further decrease of polarity (Figure 3b) in the inverted region does not change this tendency because both the decrease of reorganization energy and the increase of the reaction free energy lead to increased activation free energy.

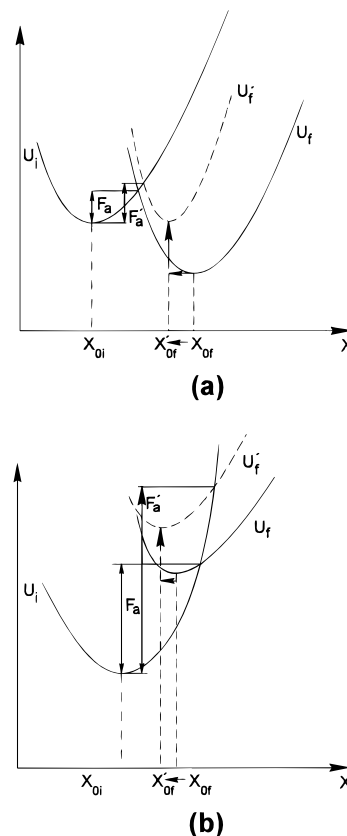


Figure 3. Shift of the Gibbs free energy surface of the final state ($U_f \rightarrow U_f'$) with the decrease of the static dielectric constant for the reaction of charge separation, eq 27: (a) normal region, (b) inverted region.

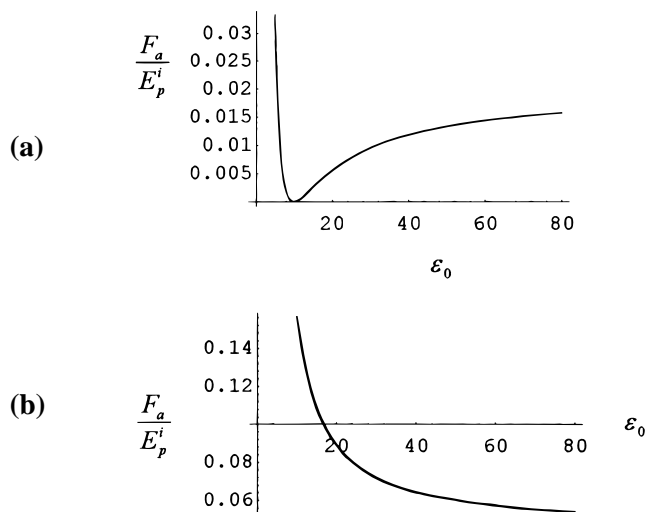


Figure 4. Dependence of the activation Gibbs free energy F_a on the static dielectric constant for charge recombination (eq 25) in units of $E_p^i = 1/8\pi\epsilon_0 \int d^3r D_f^2$. (a) Transition from the normal to inverted region. The decrease of the dielectric constant leads to a decrease of the activation Gibbs free energy F_a in the normal region, but to an increase of F_a in the inverted region. (b) Behavior in the inverted region.

A striking difference is faced for the reaction 25 in the exothermic regime. The medium polarity decrease here affects the free energy surface configuration, as shown in Figure 2a,b. Further decrease of polarity in the inverted region will revert the tendency, compared to the normal region: both the reorganization and reaction free energies decrease here, and this leads to an increase of the activation free energy (Figure 4b).

The discussion above shows that the effect of the continuum medium polarization on the reaction rate favors in certain cases

reactions in a solid with lower dielectric constant. Note, however, that macroscopic electrostatics, employing the bulk values of the dielectric constant of the solvent, was used in eqs 21, 24, 26, and 28. More sophisticated approaches use the nonlocal electrostatics,^{58,59} which is a way to parametrize the microscopic effect in electrostatic interactions. Nonlocal electrostatics rests on dielectric functions with spatial dispersion instead of simply dielectric constants. Implications of this approach are considered in the next section.

Generally, there is no direct relation between the changes in the intramolecular structure of complex reactants, which may accompany the charge transfer and the properties of the medium. However, the structure and dynamics of the first solvation shell, which is often treated as discrete, do depend on the properties of the medium. For example, aqua complexes of, say, lanthanoid metals, can have rather weak bonds for the water molecules of the first solvation shell, the structure of which undergoes considerable reorganization in electron transfer. This adds to the total reorganization energy and decreases the rate. Estimations show that the increase of the reorganization energy can amount 20%.^{24,60} The crystal structure of solids is more rigid, and if the reactants fit the structure, the reorganization of the local surroundings would be smaller. The situation here is more similar to metal complexes with rigid structures of the type $[\text{Fe}(\text{CN})_6]^{3-/4-}$ or $\text{MnO}_4^{1-/2-}$. In contrast, if the reactants do not fit the crystal structure, they may cause a mechanical tension of the solid. Different tension, before and after reaction (e.g., due to the change of the size of the reactants) will contribute to reorganization energy, thus lowering the rate constant.⁶¹

A quite different situation is encountered in nonequibrated solids (e.g., glasses). Appropriate charge rearrangement may here release the energy of local mechanical tensions. This will contribute to the heat of reaction, increasing the reaction rate. The energy released in the relaxation may be absorbed by other reaction pairs, which would stimulate chain reactions.^{61,62}

Subtler Effects: Do They Change the Picture?

Effects of Spatial Dispersion. Calculation of the reorganization energy is usually split in two parts: contribution from the local modes and contribution from the dielectric polarizability. The former is calculated via the standard routine (eq 17) for parabolic potential energy surfaces which requires only the discrete mode frequencies and the coupling constants. The situation is more complicated when there is also a collective mode contribution, due to dielectric polarizability. The use of classical electrostatics here, as in the derivation of the Marcus formula (eq 21),⁶ is in principle questionable because it is applied to electric fields of microscopic charge sources (i.e., ions or molecular reactants). When the size of the corresponding charge distributions is comparable with the characteristic structure distances of the medium, the spatial dispersion of the dielectric response should, strictly speaking be taken into account (i.e., nonlocal electrostatics should be used^{58,59,63,64}).

Nonlinear response effects could also be important for small ions.⁶⁵ There is no general framework for these effects, except for heuristic modifications of the primitive macroscopic electrostatic model. Case microscopic calculations are more instructive and justified here. Note that in application to electron transfer kinetics we are mainly interested in the response to the field of a single transferable electron in the initial and final state. If the radius of localization of this electron is sufficiently large (>2 Å), nonlinear effects would be small. If the reactants themselves are multiply charged, the response to their field is of course nonlinear. This may be accounted for either by introducing a new effective medium around the reactants, or

by incorporating the first solvation shell into the reactant subsystem. Below we ignore nonlinear response effects, and focus on effects due to spatial dispersion.

The constitutive relation of nonlocal electrostatics,⁵⁹

$$D_{\alpha}(\vec{r}) = \sum_{\beta} \int d\vec{r}' \epsilon_{\alpha\beta}(\vec{r}, \vec{r}') E_{\beta}(\vec{r}') \quad (29)$$

defines the nonlocal dielectric tensor $\epsilon_{\alpha\beta}(\vec{r}, \vec{r}')$, the dependence of which on spatial coordinates \vec{r}, \vec{r}' accounts for the limitations on the dielectric response at short-range scales, imposed by the structure of the medium. For homogeneous media $\epsilon_{\alpha\beta}(\vec{r}, \vec{r}') = \epsilon_{\alpha\beta}(\vec{r} - \vec{r}')$, and it is convenient to use the Fourier transform of this function from the real to wave vector space $\epsilon_{\alpha\beta}(\vec{k})$. Only the longitudinal component of this tensor $\epsilon(k) = \sum_{\alpha\beta} \epsilon_{\alpha\beta}(\vec{k}) (k_{\alpha} k_{\beta} / k^2)$ would, moreover, appear in electrostatics if the medium is isotropic. For the inertial polarization this gives the relationship

$$P_{\parallel \vec{k}} = C(k) D_{\parallel \vec{k}}$$

where

$$C(k) = \frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon(k)} \quad (30)$$

is the response function which is different for different \vec{k} -Fourier components. When the spatial dispersion is negligible, $\epsilon(k) = \epsilon_0$ in a nonconductive medium where $C(k) = C \equiv 1/\epsilon_{\infty} - 1/\epsilon$ is the Pekar parameter.²

The reorganization free energy for electron transfer between the microscopic reactants is the quantity for which the nonlocal effects may be most significant. General expressions for E_r are available and rest on the assumption that the reactants do not disturb the medium which remains homogeneous and isotropic; the fact that part of the medium volume is occupied by the reactants is neglected. This is, of course, a strong idealization, but it works fairly well, because it interpolates between two limiting cases.^{58,59} Indeed, in the absence of nonlinear effects the volume occupied by ions is small for small ions, for which the spatial dispersion effects are particularly significant. For large ions this volume is large, but the spatial dispersion effects are now small. The expression for E_r reads^{59,64,66}

$$E_s = \frac{1}{8\pi} \int d^3k C(k) |\vec{D}_i(\vec{k}) - \vec{D}_f(\vec{k})|^2 \quad (31)$$

where $D(k)$ are the Fourier components of the inductions.

This expression takes a particularly simple form in the case of a symmetric electron exchange between two ions of the same size, modeled as charged Born spheres,

$$E_r = \frac{2e^2}{\pi} \int_0^{\infty} dk C(k) \frac{\sin^2 ka}{k^2 a^2} \left(1 - \frac{\sin kR}{kR} \right) \quad (32)$$

where a is the Born radius of the ions and R the distance between their centers. When spatial dispersion is absent, $\epsilon(k) = \epsilon_0$, and this equation reduces to the Marcus formula (eq 21).

For symmetric reactions, the free energy of reaction vanishes, so that $E_a = E_r/4$. In liquid electrolytes, the picture is complicated by work terms. The probability of reactants approach ($\Phi(R)$, eq 2) would be proportional to $\exp(-F(R)/k_B T)$, where $F(R)$ is the Free energy of interaction between the reactants as a function of distance. When both reactants are charged, the work term is dominated by electrostatic interaction. For "Born ions" (of radii a_1 and a_2 and charges e_{z1} and e_{z2})

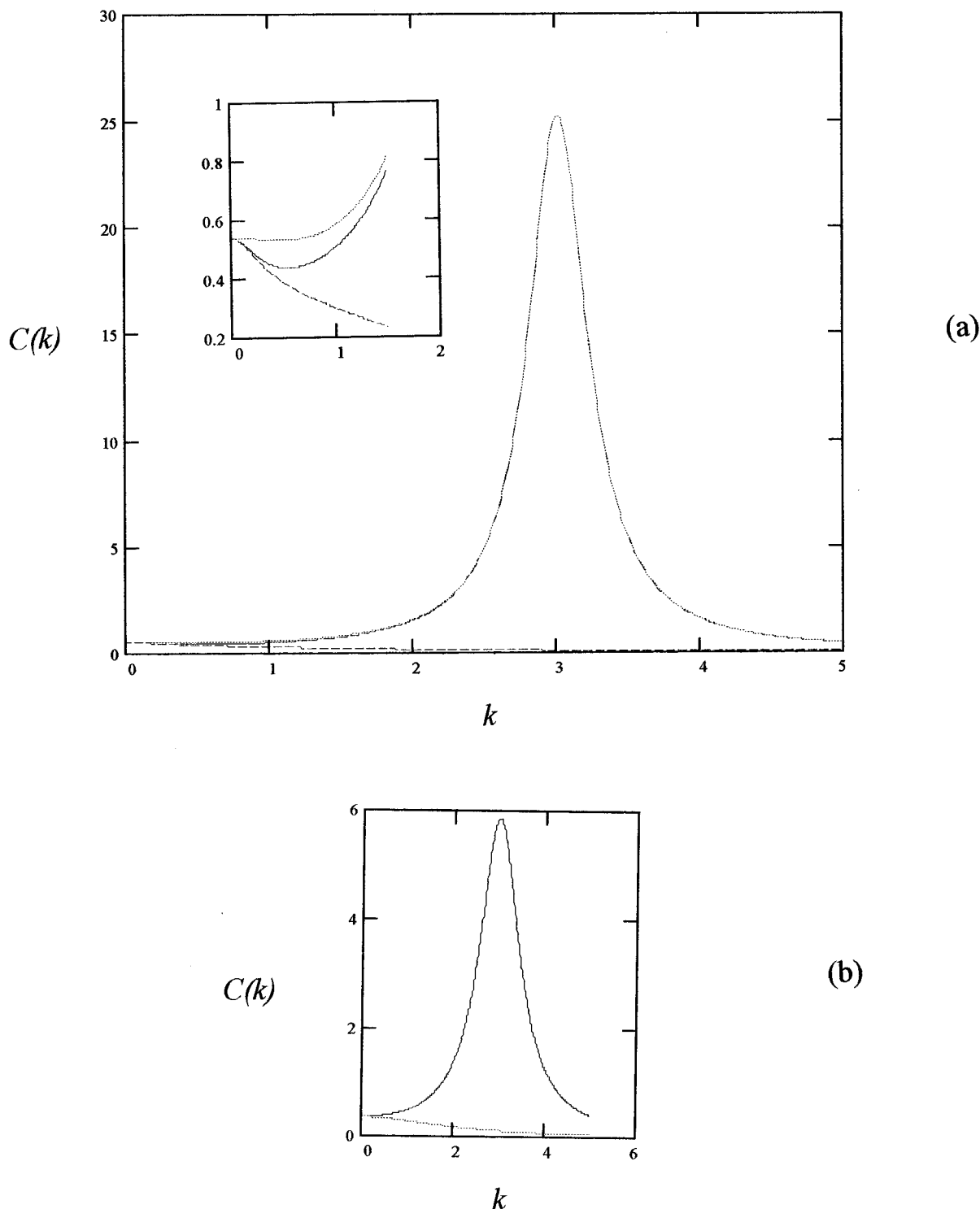


Figure 5. Dependence of the response function $C(k)$ on the wave vector k , calculated according to eq 35: (a) $\epsilon_\infty = 1.8$, $\epsilon^* = 4.9$, $\epsilon_0 = 80$; solid line, $\Lambda = 3 \text{ \AA}$, $\lambda = 0.33 \text{ \AA}$, $l = 0.33 \text{ \AA}$, $L = 0.6577 \text{ \AA}$; dotted line, $\Lambda = 1 \text{ \AA}$, $\lambda = 0.33 \text{ \AA}$, $l = 0.33 \text{ \AA}$, $L = 0.6577 \text{ \AA}$ (the difference between the solid and dotted lines can be seen only at small k , see insert); dashed line, $\Lambda = 3 \text{ \AA}$, $\lambda = 0.5 \text{ \AA}$, $l = 0 = L$ (the Lorentzian, given by eq 34). (b) $\epsilon_\infty = 1.8$, $\epsilon^* = 4.9 = \epsilon_0$, solid line, $\lambda = 0.33 \text{ \AA}$, $l = 0.33 \text{ \AA}$, $L = 0.65 \text{ \AA}$; dotted line (Lorentzian limit), $\lambda = 0.5 \text{ \AA}$, $L = 0$.

$$F(R) = \frac{2e^2 z_1 z_2}{\pi} \int_0^\infty \frac{dk}{\epsilon(k)} \frac{\sin ka_1}{ka_1} \frac{\sin ka_2}{ka_2} \frac{\sin kR}{kR} \quad (33)$$

Now if we know the form of $\epsilon(k)$, we may calculate these integrals. However, there is no common view on the shape of $\epsilon(k)$ for polar liquids, because experimental information has only become available very recently,⁶⁷ but is still incomplete. Initially, the Lorentzian approximation for $\epsilon(k)$ was used, derived on the basis of the phenomenological Landau Hamiltonian with a gradient expansion in polarization fluctuations. For $C(k)$ it

reads⁶⁸

$$C(k) = \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon^*} \right) \frac{1}{1 + \lambda^2 k^2} + \left(\frac{1}{\epsilon^*} - \frac{1}{\epsilon_0} \right) \frac{1}{1 + \Lambda^2 k^2} \quad (34)$$

where λ and Λ are the correlation lengths of the librational and orientational polarizations, respectively, and ϵ^* is the dielectric constant in the frequency range which separates librational and orientational motions. The response to the field components with fast variation in space is thus impeded, as the domains of coherence ($\sim \Lambda, \lambda$) are unable to respond to such components.

Statistical mechanical calculations and molecular dynamic computer simulations of $\epsilon(k)$ have shown more complicated shapes,^{67–75} associated with damped oscillations of correlation functions in real space. The corresponding $C(k)$ has a peak at intermediate value of k which reflects the wave number of these oscillations which, for brevity, we call the “spatial resonance”. For water this resonance form was supported by the analysis of neutron diffraction data on the partial structure factors, O–O, H–H, and O–H.⁶⁷ The resonance shape is roughly reproduced by a more general expression than eq 34, derived on the basis of an effective Hamiltonian which predicts damped oscillations in the correlation functions,⁷⁶

$$C(k) = \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon^*}\right) \frac{1}{1 + \lambda^2 k^2 - \frac{L^2 k^2}{1 + l^2 k^2}} + \left(\frac{1}{\epsilon^*} - \frac{1}{\epsilon_0}\right) \frac{1}{1 + \Lambda^2 k^2} \quad (35)$$

Here the second term describes the response of the low-frequency part of the orientational polarization, while the first term is due to librational motions coupled with the hydrogen bond density fluctuations. There are two parameters which are new with regards to eq 34. These are l , the correlation length of the local density fluctuations, and the length L ($< l + \lambda$) proportional to the coupling constant that binds the fluctuations of polarization with the fluctuations of local density gradients. With $L = 0$ this equation reduces to the Lorentzian form (eq 34). The dispersionless limit is obtained at $\lambda = \Lambda = L = 0$.

Figure 5 shows $C(k)$ for these two approximations. The values used for λ and l in Figure 5a approach reproduction of the simulation and diffraction data for water.⁶⁷ The best fit values seem, however, to be too small to be correlated with any molecular or even group dimensions, but can presently be treated simply as fitting parameters. In Figure 5b, we have shown a hypothetical example for a low-polar medium without hydrogen bonding. $\epsilon(k)$ of Lorentzian shape has been obtained for solid insulators and semiconductors with the use of band structure calculations.^{77–79} For $C(k)$ this corresponds to eq 34 with $\Lambda = \lambda \sim 1$ Å.

Reorganization free energies calculated with the use of eq 35 are shown in Figure 6. The analytical expression is voluminous and available elsewhere (cf. Appendix B of ref 76), but reduces to the following form in the Lorentzian limit⁶³

$$E_r = e^2 \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon^*} \right) \left\{ \frac{1}{a} \varphi\left(\frac{2a}{\lambda}\right) - \frac{1}{R} \left[1 - \Phi\left(\frac{2a}{\lambda}\right) \right] e^{-R/\lambda} \right\} + e^2 \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon^*} \right) \left\{ \frac{1}{a} \varphi\left(\frac{2a}{\Lambda}\right) - \frac{1}{R} \left[1 - \Phi\left(\frac{2a}{\Lambda}\right) \right] e^{-R/\Lambda} \right\} \quad (36)$$

where

$$\varphi(x) = 1 - \frac{1}{x} (1 - e^{-x}) \quad (37)$$

$$\Phi(x) = 2 \frac{\cosh(x-1)}{x^2} \quad (38)$$

The three curves in Figures 6a,b correspond to $\epsilon(k)$ with the resonance structure, which mimics the data for water, to the Lorentzian approximation, and to the dispersionless limit (for which the reorganization free energy is given by the Marcus formula). Figure 6a shows E_r as a function of the distance between the reactants, $d = R - 2a$, while Figure 6b displays the dependence on reactant radius, a , for the two reactants in contact (i.e., at $d = 0$). Figure 6c shows the reorganization free energy for the model in which the Born spheres of the

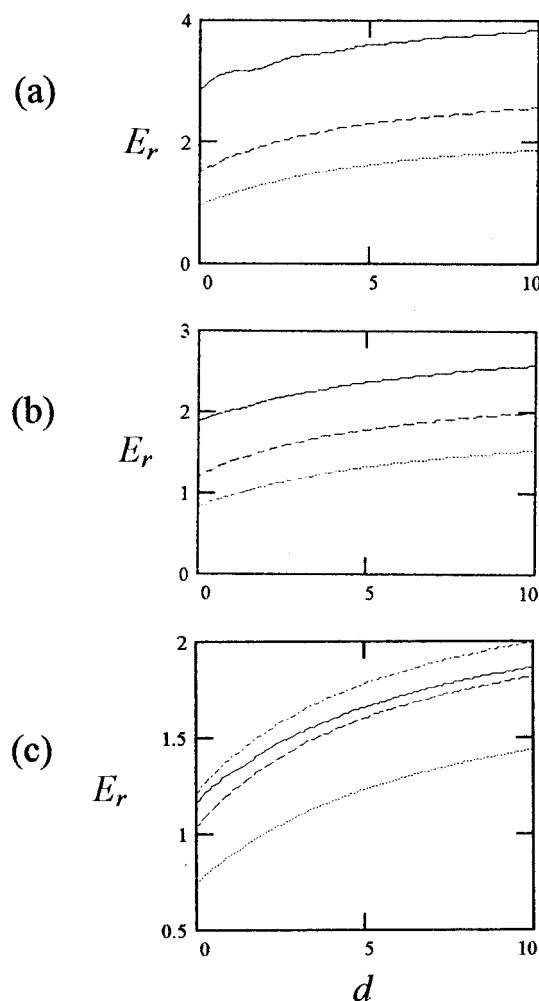


Figure 6. The dependence of the reorganization Gibbs free energy (in eV) on the distance between the identical reactants, $d = R - 2a$, Å. Calculated for the Born sphere model of the reactants (eq 32) with $a =$ (a) 2.4 Å, (b) 3 Å, and (c) for the smeared Born spheres⁶⁴ (for which the factor $(\sin^2 ka)/(k^2 a^2)$ in the integrand of eq 32 should be replaced by the square of the charge density formfactor given by eq 12 of ref 84 with a smearing parameter $\eta = 0.3$ Å). The curves correspond to different forms of $C(k)$. Spatial-resonance approximation, — (solid line of Figure 5a); dispersionless limit, - - -; Lorentzian form, ... (dotted line of Figure 5a); dash-dotted line in (c) corresponds to the Marcus formula, derived for the Born model of reactants.

reactants are smeared out (see the text under the Figure 6). The dependence of the reorganization energy on the reactant radii is presented in Figure 7, demonstrating the effect of smearing. The Marcus result lies between the resonance case and the Lorentzian approximation which gives the lowest reorganization free energy. The ability of the medium polarization to reorient in the course of electron transfer is reduced in the Lorentzian approximation because of the strong orientational correlations in space. This is seen particularly well from the limiting case of eq 36, at $\lambda = 0$ and $\Lambda \gg a$:

$$E_r \approx e^2 \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon^*} \right) \left(\frac{1}{a} - \frac{1}{R} \right) + e^2 \left(\frac{1}{\epsilon^*} - \frac{1}{\epsilon_0} \right) \left[\frac{1}{\Lambda} - \frac{1}{R} (1 - e^{-R/\Lambda}) \right] \quad (39)$$

The larger is the correlation coherence domain (larger Λ), the smaller E_r . This is different for the resonance approximation. The spatial dispersion leads here not to smaller but much higher values of the response function. This effect is called overscreening.^{80,81} At $k = 0$ the response includes the contribution from all wavelengths and cannot be larger than $1/\epsilon_\infty$. At given

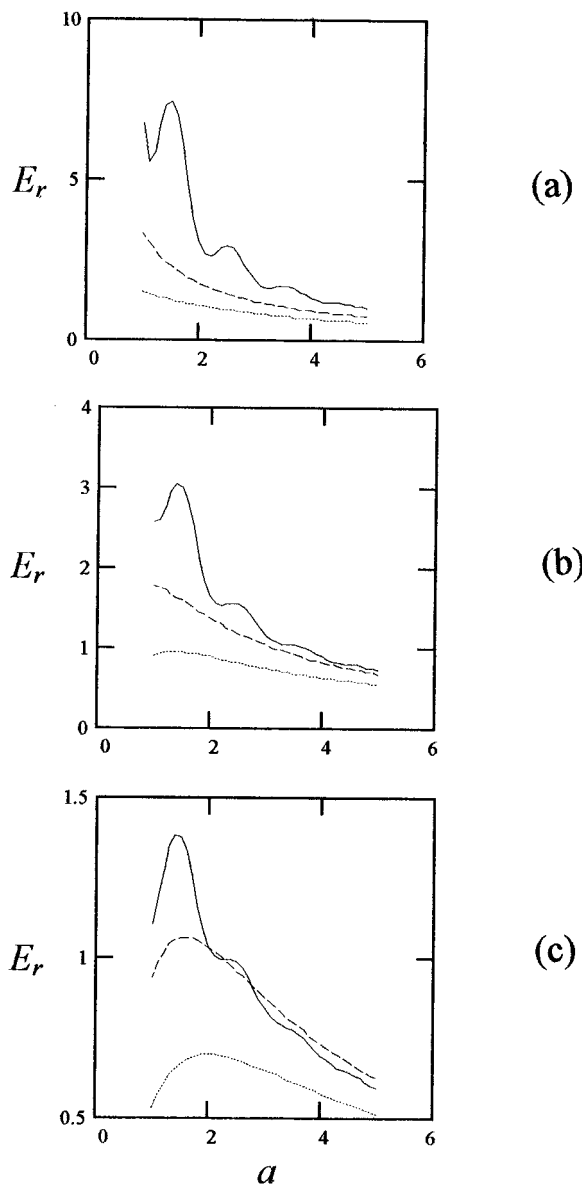


Figure 7. The dependence of the reorganization Gibbs free energy (in electron volts) on the radius of the reactants a (in angstroms), at the contact distance $d = 0$. The curves correspond to different approximations for $C(k)$: Spatial-resonance approximation, — (solid line of Figure 5a); dispersionless limit, - - , Lorentzian form, ... (dotted line of Figure 5a). Variation of the charge smearing parameter, $\eta =$ (a) 0 Å, (b) 0.3 Å, (c) 0.5 Å.

“resonant” values of k it can, however, be very large, and E_r is therefore larger. The Marcus formula does not take into account any structure in correlations, and therefore falls between these two cases. Both in the Marcus and Lorentzian cases, E_r is a monotonously decreasing function of the reactant size a . This is not the case, however, for the resonance approximation which shows oscillations superimposed on the decaying background. Figure 7 shows maxima at $a = 1.4$ and 2.4 Å. This is the reason why in Figure 6b the solid line for E_r is lower than the one in Figure 6a, even though the radius is larger for the former. Figure 7 shows the depression of oscillations by smearing of the ionic charge distribution.

The shape of $\epsilon(k)$ has a strong effect on the electrostatic interaction (eq 33). It was shown that approximations of the resonance type lead to oscillations of the screened potential^{74,76} (cf. ref 82), so that ions of the same sign may approach each other to short distances since their repulsion is considerably depressed.^{83,84} The spatial dispersion in the Lorentzian ap-

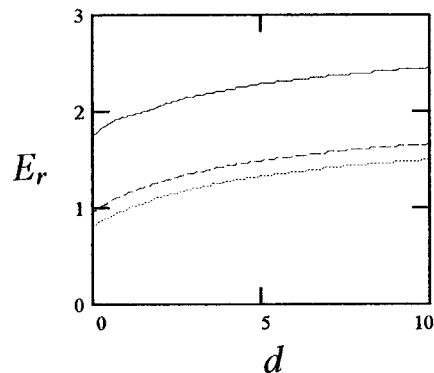


Figure 8. The dependence of the reorganization Gibbs free energy on the inter-reactant distance d . Spatial-resonance approximation, — (solid line of Figure 5b); dispersionless limit (Marcus equation) - - ; Lorentzian form, ... (dotted line of Figure 5b).

proximation drastically enhances the repulsion.^{58,59,84} The limitations on the mutual approach of the similarly charged reactants would thus be much weaker in a liquid than in a solid.

It makes sense to compare also the response of solids and liquids for low-polarity liquids. Molecular statistical-mechanical calculations show that the resonant shape (Figure 5b) is also typical for low polar fluids,⁸⁵ whereas for ionic crystals we may seemingly use the Lorentzian approximation.^{77,86} Figure 8 shows the dependence of the reorganization free energy on the interreactant separation d . We see that E_r is considerably larger in the liquid than in the solid state.

Inhomogeneities: Interfaces and Cavities. The discussion in the preceding sections rested on the assumption that the reaction medium is a uniform dielectric. However, the presence of the reactants themselves creates inhomogeneities in the dielectric. Due to their finite sizes, they may form cavities with dielectric properties quite different from the properties of the outer medium. Another type of inhomogeneity is encountered in reactions at the interface between two dielectric media (e.g., two immiscible liquids). In both cases the situation is much more complicated than for uniform media. The physical meaning of the reorganization free energy and ways of calculation of this important quantity for nonuniform media have been discussed.^{87–90} Problems are associated with the fact that the inertial polarization reorganization free energy must be calculated. We, therefore, have to separate the inertial and fast, inertia-less polarization, where the latter follows adiabatically the electron motion and does not create a potential barrier for the reaction. This separation is simple in uniform media, but it requires more careful analysis in nonuniform media.

By its physical meaning, the reorganization energy is the free energy required to change the inertial polarization from its initial to its final equilibrium value, provided the electron remains at the donor molecule. It is thus necessary to know how the equilibrium values of the polarization are related with the initial and final charge and field distributions. The key point here is the understanding that the inertial and inertia-less polarizations are independent quantities, and as such, they are, generally, in different equilibrium fields, although they originate from the same charge distribution. The fast polarization is at equilibrium with the field of the electron in the medium provided that all slow motions are frozen; the dielectric constant of such an effective medium is ϵ_∞ . The inertial polarization in the initial and final states is, on the other hand, at equilibrium with the fields aroused by the electron clouds in the medium in which all modes are active (i.e., in a medium with the dielectric constant ϵ_0). The reorganization free energy may then be calculated as the difference of the electrostatic free energies in

these two media:

$$E_r = \frac{1}{8\pi\epsilon_\infty} \int d^3 r (\vec{D}_i - \vec{D}_f)_{\epsilon_\infty}^2 - \frac{1}{8\pi\epsilon_0} \int d^3 r (\vec{D}_i - \vec{D}_f)_{\epsilon_0}^2 \quad (40)$$

where the subscripts denote the electrostatic inductions calculated in the medium having the corresponding dielectric constant. The inductions are independent of the dielectric constants of the media and coincide with each other and with the “vacuum” field (i.e., with the field in the absence of the medium) only in some special, although representative cases.⁹¹ Equation 40 then reduces to eq 21 for uniform media. Generally, difference of values calculated by eqs 40 and 21 may be significant.^{89,92}

Taking into account the spatial dispersion of the slow polarization, while neglecting it for the fast polarization, eq 40 may be extended to

$$E_r = \frac{1}{8\pi\epsilon_\infty} \int d^3 r (\Delta \vec{D})_{\epsilon_\infty}^2 - \frac{1}{8\pi} \int d^3 r \int d^3 r' \sum_{\alpha, \beta} \Delta \vec{D}_\alpha|_{\epsilon(r, r')}(\vec{r}) \epsilon_{\alpha\beta}^{-1}(\vec{r}, \vec{r}') \Delta \vec{D}_\beta|_{\epsilon(r, r')}(\vec{r}') \quad (41)$$

where $\Delta \vec{D} = \vec{D}_i - \vec{D}_f$, and $\epsilon_{\alpha\beta}^{-1}(\vec{r}, \vec{r}')$ is the inverse static dielectric tensor. Although formally simple, eq 41 involves the kernel $\epsilon_{\alpha\beta}^{-1}(\vec{r}, \vec{r}')$, the inverse integral operator of which, posing a separate problem, can be determined for a given $\epsilon_{\alpha\beta}(\vec{r}, \vec{r}')$. The latter is not known experimentally, but it can be reasonably approximated. As a result, the second integral in eq 41 may be calculated only in simplified models.

Such models were employed for the calculation of the reorganization free energy of electron transfer reactions at metal electrodes.^{93,94} Account of spatial dispersion has led to unusual dependencies of the reorganization free energy on the electron transfer distance. Counterintuitively the reorganization free energy *rises* with decreasing transfer distance, which is due to effects of field penetration into the metal on the image forces.^{95,96} Such results do not lead to a Marcus-like relation for the rate constants between the homogeneous and electrode reactions.⁹⁷ These results did not, however, take into account the difference between $\Delta D|_{\epsilon_0}$ and $\Delta D|_{\epsilon(r, r')}$ in eq 41, and this analysis should be revisited.

Reorganization Energy of the Environment for Reactions in Electrolytes: Effects of the Ionic Atmosphere

Charge transfer processes in electrolyte solutions of finite ionic strength are accompanied by reorganization of both the pure medium polarization and of the ionic atmosphere. This makes the calculation of the rate constant and reorganization energy more complex, not only technically, but also conceptually,⁹⁸ because Debye screening cannot be straightforwardly incorporated into the corresponding values of the electrostatic induction.

We consider, for example, the symmetric electron exchange reaction, between otherwise neutral species, $A^- + A \rightarrow A + A^-$ and represent the ionic atmosphere by a single positive ion C which is shifted from one reactant to the other in the reaction. (This tutorial model mimics processes in weakly polar solvents where ion pairs dominate⁹⁹). For the sake of clarity, the potential energy of the ion C will be modeled by the diabatic parabolic potential energy curves

$$U_i(R) = \frac{1}{2} M \Omega^2 (R - R_{0i})^2$$

$$U_f(R) = \frac{1}{2} M \Omega^2 (R - R_{0f})^2 \quad (42)$$

where M is the mass of the ion, Ω the vibrational frequency, and R_{0i} and R_{0f} the equilibrium positions of the ion C in the initial and final states.

Similarly, the polarization of the medium will be modeled by a single-harmonic oscillator

$$U_i(q) = \frac{1}{2} m \omega^2 (q - q_{0i})^2$$

$$U_f(q) = \frac{1}{2} m \omega^2 (q - q_{0f})^2 \quad (43)$$

where q is the effective normal coordinate.

Due to the compensation of the electric field of the electron by the ion C, the polarization of the medium in the initial and final equilibrium configurations q_{0i} and q_{0f} are small. However, the medium polarization depends on the position of the ion C (i.e., q_{0i} and q_{0f} depend on R). The simplest linear dependence emerges if the interaction energy between the ion and polarization is $\sim Rq$, that is

$$q_{0i}(R) = q_{0i} - \nu R$$

$$q_{0f}(R) = q_{0f} - \nu R \quad (44)$$

Transition occurs at the saddle point $\{R^*, q^*\}$ on the crossing of the two-dimensional potential energy surfaces (Figure 9)

$$U_i(R, q) = \frac{1}{2} M \Omega^2 (R - R_{0i})^2 + \frac{1}{2} m \omega^2 (q - q_{0i})^2$$

$$U_f(R, q) = \frac{1}{2} M \Omega^2 (R - R_{0f})^2 + \frac{1}{2} m \omega^2 (q - q_{0f})^2 \quad (45)$$

The transitional configuration for this symmetric reaction is given by

$$R_* = \frac{R_{0i} + R_{0f}}{2}$$

$$q_* = \frac{q_{0i}(R_*) + q_{0f}(R_*)}{2} \quad (46)$$

We divide the two-dimensional motion toward the transition configuration in two steps, viz. the motion of the ion from R_{0i} to R_* and the subsequent motion along q from $q_{0i}(R_*)$ to q_* . The work spent in these two steps is calculated by substitution of eqs 46 into eq 45.

$$F_a = (1/4)(1/2) m \omega^2 [q_{0f}(R_*) - q_{0i}(R_*)]^2 + (1/4)(1/2) M \Omega^2 (R_{0f} - R_{0i})^2 \quad (47)$$

This is one quarter of the total reorganization free energy which is the sum of the medium E_s and ion E_{ion} terms

$$E_s = \frac{1}{2} m \omega^2 [q_{0f}(R_*) - q_{0i}(R_*)]^2$$

$$E_{ion} = \frac{1}{2} M \Omega^2 (R_{0f} - R_{0i})^2 \quad (48)$$

Substitution of eq 44 into eq 48 shows that the result for E_s is the same as that in the absence of the ion ($\nu_i = \nu_f = 0$). This is because the reorganization of the medium is calculated for

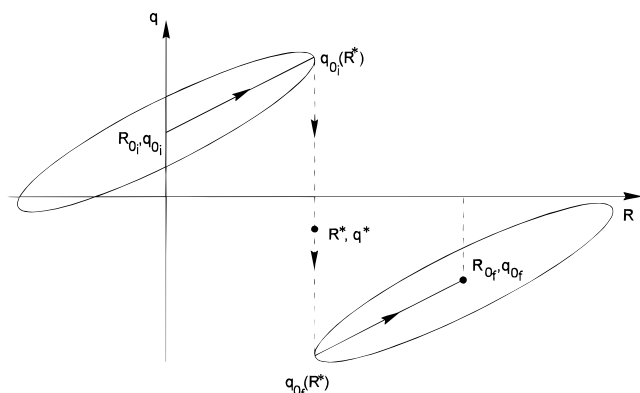


Figure 9. The initial and final Gibbs free energy surfaces for electron transfer reaction in the presence of ionic atmosphere: the cross sections by planes of constant free energy. R is the coordinate of an ion modeling the ionic atmosphere (see the text). q is the coordinate which describes the polarization of the medium. q_{0i} , R_{0i} and q_{0f} , R_{0f} are the initial and final equilibrium values. The small value of $|q_{0f} - q_{0i}|$ reflects the screening by the ionic atmosphere. q^* and R^* are the coordinates of the transition configuration. The equilibrium $q_{0i}(R)$ and $q_{0f}(R)$ values of the polarization depend on R : $|q_{0f} - q_{0i}|$ increases upon the shift of the ions towards the transition configuration R^* .

the electron hop from the donor to acceptor at a *fixed* position of the ion C, but not for the shift of the electron and the ion charge between the equilibrium initial and final positions. In the latter case the shift of the ion would almost fully compensate the field of the electron and close the difference between q_{0i} and q_{0f} .

Even though the medium reorganization energy is unaltered by the ion, a direct contribution from the ion remains, cf. eqs 48. Different approaches may be used for the evaluation of this contribution.

1. A general approach to the contribution of the ionic atmosphere was formulated in ref 98. Closed form expressions were obtained in refs 100–102 in the Debye–Hückel approximation:

$$E_{\text{ion}} = \frac{e^2}{\epsilon_0} \left[\frac{1}{2a} \frac{2\kappa a}{1 + \kappa a} + \frac{1}{R} \left(\frac{e^{-\kappa(R-a)}}{1 + \kappa a} - 1 \right) \right] \quad (49)$$

where R is the interreactant distance, a the radius of each reactant, and $\kappa = \sqrt{8\pi z^2 e^2 / \epsilon_0 k_B T}$, the inverse Debye length. Equation 49 shows that the reorganization free energy of the ionic atmosphere *rises* with increasing κ (i.e., with the increase of the ionic concentration). An upper estimate for two ions of radius $a = 2$ Å in contact and 1 M electrolyte concentration ($1/\kappa = 3$ Å) is given by

$$F_{\text{ion}} = \frac{14}{\epsilon_0} k_B T \frac{\frac{6}{\epsilon_0} - 1 + e^{-6/\epsilon_0}}{\frac{6}{\epsilon_0} + 1} \quad (50)$$

For water ($\epsilon_0 \approx 83$) this contribution is negligibly small ($\approx 0.2 k_B T$) but could reach values $\sim 5 k_B T$ for a solid electrolyte ($\epsilon_0 \approx 10$).

2. The contribution of the ionic atmosphere may also be calculated with the help of nonlocal electrostatics. For simplicity we consider here spatial dispersion only due to the ionic atmosphere and neglect the wave vector dependence of the solvent dielectric constant. Then,⁸⁶

$$\epsilon(k) = \epsilon_0 + \frac{\kappa^2}{k^2} \quad (51)$$

and eq 32 gives

$$E_{\text{rk}} = \frac{e^2}{\epsilon_0} \left\{ \frac{1}{a} \left[1 - \frac{1}{2\kappa a} (1 - e^{-2\kappa a}) \right] - \frac{1}{R} \left[1 - \frac{1}{2\kappa^2 a^2} (\cosh 2\kappa a - 1) e^{-\kappa R} \right] \right\} \quad (52)$$

The validity of eq 51 and 52 is the same as of the Debye–Hückel approximation, except that eq 51 does not take into account the finite size of electrolyte ions, whereas eq 52 does. The contribution of the ionic atmosphere to the reorganization free energy, calculated by eqs 49 and 52, as a function of inverse Debye length (square root of ionic concentration) is shown in Figure 10. These two equations give closely related results, although there is some quantitative difference because the nonlocal electrostatic approach in its present form does not take into account the finite size of the ions.

Another, more general form of the reorganization free energy, valid also for nonuniform dielectrics is

$$E_r = \frac{1}{8\pi} \frac{1}{\epsilon_\infty} \int d^3r (D_i - D_f)_{\epsilon_\infty, \kappa=0}^2 - \frac{1}{8\pi} \int d^3r (E_i - E_f)(D_i - D_f)_{\epsilon_0, \kappa} \quad (53)$$

Here, E_r is the total reorganization free energy which includes the contributions of both the medium polarization and the ionic atmosphere. The first term on the right-hand side (rhs) is nothing else than the free energy of electric field, produced by the difference of the charge distributions of initial and final states, in the fast (inertialess) environment (i.e., neither the ions nor the slow polarization contribute). The second term is the electrostatic free energy in the environment including both slow and fast components (polarization and ions both contribute here). Note that the electric fields in each term are calculated in different environments and are therefore different. Only in a homogeneous medium (without cavities or other boundaries) and in absence of ionic atmosphere eq 53 does reduce to the generalization of the Marcus formula by eq 32, because in this case the electric inductions are independent of the dielectric constant of the medium and $D = \epsilon E$. For a uniform medium with ions, the rhs of eq 53 is the sum of the terms given by eqs 21 and 49.

The conclusion from this section is thus at first glance counterintuitive: the ionic atmosphere does not reduce but increases the reorganization. The absolute value of the enhancement is small for highly polar media, but may be significant for low-polar media, including solid electrolytes. This does not mean, of course, that mobile ions always impede the reaction rates. Other factors are also important. Cases where both reactants are likely charged or one is neutral must be distinguished. In the latter case the effect of ionic atmosphere impedes the reaction. In the former, the ionic atmosphere helps the reactants to approach each other, and this effect facilitates the reaction and generally dominates over the impeding effects of the reorganization free energy.

Preexponential Factor

The preexponential factor has rather different forms for adiabatic and diabatic reactions.

The diabatic preexponential factor is determined *both* by the velocity of the motion along the nuclear coordinates near the

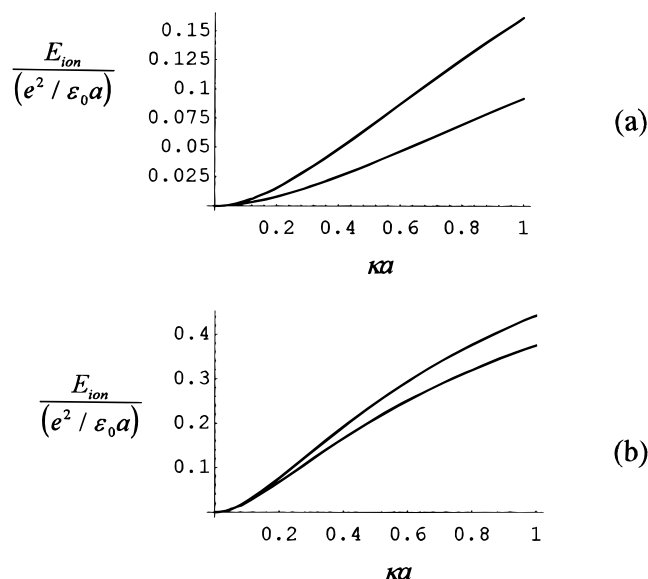


Figure 10. The reorganization Gibbs free energy of the ionic atmosphere as a function of the inverse Debye length κ at different interreactant distances R . (a) $R = 2a$, (b) $R = 8a$. Upper curves, Lorentzian approximation (eq 51), lower curves, Debye-Hückel approximation (eq 49).

transition configuration and the probability of electron transition. The factor has approximately the form of the product of the ratio of the corresponding characteristic times and the effective vibrational frequency ω . The nuclear characteristic time τ_n can be expressed in terms of the reorganization energy E_r , the thermal energy $k_B T$, and ω (i.e., $\tau_n \sim V/(\omega\sqrt{k_B T E_r})$). Here, $\omega\sqrt{E_r}$ describes the difference of the slopes of the potential energy surfaces at their crossing and $\sqrt{k_B T}$ is proportional to the average thermal velocity. The electronic time, $\tau_e \sim \hbar/V$. (Eq 18 coincides in fact with the ratio $\tau_n/\tau_e^{10,52}$). The preexponential factor is thus smaller, the larger the reorganization energy. We may therefore expect an increase of the preexponential factor when moving from the liquid to the solid state.

The electronic transition matrix element V depends largely on the local structure, which can of course vary strongly from system to system.^{103,104,105} In some cases the solid matrix may provide a smaller equilibrium distance between the reactants (or between the reactant and electrode surface), thus facilitating the wave function overlap for the transferable electron or proton. A further interesting difference is that reactants in liquid solutions are usually solvated and the mutual approach of the reactants may require deformation or partial disintegration of their solvation shells, whereas ions in solid electrolytes move without solvation shell and may, in principle, approach each other more closely.

The character of *adiabatic transitions* is different due to resonance splitting of the free energy surfaces. Transition from the initial to final state is here along a single (i.e., the lower free energy surface). The activation barrier is reduced, as compared to the diabatic limit, but all other tendencies remain.^{10,106,107} However, the physical properties of the preexponential factor are entirely different. The transmission coefficient is unity and the preexponential factor A_{ad} involves only an effective frequency ω_{eff} (see eq 1). The latter depends in general on vibrational and relaxation characteristics of both the medium and the reacting molecules. In liquids characterized by the Debye dielectric loss spectrum the effective frequency is inversely proportional to the longitudinal relaxation time τ_L ^{108–118}

$$\omega_{eff} \sim 1/\tau_L \quad (54)$$

The latter is related with the Debye relaxation time τ_D as

$$\tau_L = (\epsilon_\infty/\epsilon_0)\tau_D \quad (55)$$

The inverse relaxation time depends on the temperature in an Arrhenius-like fashion, and ω_{eff} , therefore, decreases with decreasing temperature. Note that the Arrhenius form of this dependence gives an apparent contribution to the activation energy of a few $k_B T$. Quantitatively, this compensates to some extent the resonance splitting reduction of the activation barrier, so that the resulting barrier comes close to that for diabatic transitions. Nevertheless, regarding the effects of the medium, the longer the relaxation time along the reaction coordinate, the smaller is the reaction rate.

The free energy surfaces are, however, most frequently multidimensional, as more than a single reactive mode is important. As shown in ref 118 (see also ref 116), the effective relaxation time

$$\frac{1}{\tau_{eff}} = \frac{\sum_k \frac{1}{\tau_k} E_{rk}}{\sum_k E_{rk}} \quad (56)$$

is then an appropriate quantity where E_{rk} is the reorganization free energy along a given degree of freedom. The contribution of the individual modes to the effective relaxation time is thus proportional to their weight in the total reorganization free energy, and the smaller the reorganization free energy along a given degree of freedom the smaller is its effect on the reaction dynamics. This shows how the contribution of some modes disappears upon freezing, while the reaction proceeds along other degrees of freedom.¹¹⁹

It is worth to note that eq 56 and its implications correspond to the passage over the saddle point of the multidimensional free energy surface. However, this is not always true. If the motion along a particular degree of freedom is very slow, but not totally frozen, the system will choose another path, avoiding the saddle point and going over a higher potential barrier.¹¹⁷

Organized Molecular Assemblies

Organized supramolecular systems open interesting perspectives in environmentally controlled charge transfer. Central are structurally organized layers of chainlike donor acceptor molecules. Other classes are conducting polymers and biological macromolecules. The latter incorporate conspicuously long-range electron transfer between metal centers in the secondary and tertiary structures of redox proteins and protein complexes, facilitated by large driving forces and favorable mutual organization of the centers. We consider briefly some features of these systems illustrative in the present discussion.

Synthetic Molecular Assemblies. Electron-exchanging donor-acceptor groups can be attached to chainlike molecular bridge structures of variable length and rigidity.^{37,120–124} Such molecules can be organized in two-dimensional assemblies, and photo- or field-induced electron transfer followed in solid-state^{12,125–127} or electrochemical configurations.^{128–132} The observables are current-voltage and distance relations. Environmental control is, interestingly, reflected in all the three fundamental electron transfer parameters, viz. the tunnel factor, the thermodynamic driving force, and, more putatively, the environmental reorganization Gibbs free energy.

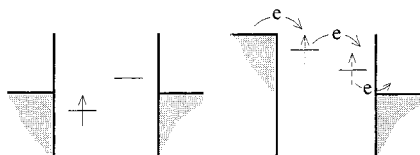


Figure 11. Schematic electronic energy level distribution for molecular donor and acceptor groups enclosed between two voltage-biased electrodes. Left: zero bias. Right: Electrode closest to the donor group biased negatively, inducing current flow. No current flow is induced on positive bias.

The tunnel factor is controlled by the distance between the donor and acceptor centres and the nature of the bridge group. Well-characterized solid systems are self-assembled mono- and multilayers of fatty acids sandwiched between metal electrodes^{12,124–127} or metallic electrodes and photoexcitable crystals such as anthracene or chloranil.^{133,134} Some of the best characterized electrochemical systems are variable-length alkyl thiols self-assembled on gold electrodes. Electrons are exchanged between the electrode and either covalently attached (say ferrocene/ferrocenium)^{129–132} or freely mobile electron transfer groups¹²⁸ by tunneling across the film. The most important observations are first that the tunnel current follows broadly an exponential distance dependence and secondly, the distance dependence can extend to many orders of magnitude corresponding to distance variations of 15–20 Å. The decay factor finally varies from small values of 0.3–0.5 Å^{−1} for photoexcitable systems to about 1.3 Å^{−1}, characteristic of many chemical and biological electron transfer systems. This difference reflects the energy gap between the conduction electrons, and the lowest antibonding orbitals of the insulating molecular barrier between the donor and acceptor regions.

Environmental control is sometimes intriguingly reflected in the current–voltage relations. These are rather featureless for direct, two-level processes where increasing bias or overvoltage lowers the activation Gibbs free energy and electron tunnel barriers. More composite information is disclosed when additional single or a pair of discrete levels are present in the tunnel region. These configurations correspond to scanning tunnel microscopy of molecular adsorbates^{135–137} or electrochemical electron transfer via adsorbates or defect states in thin films.^{138–143} As the discrete level(s) approach(es) the Fermi level of the electrode(s) resonance tunnel channels or coherent and incoherent two-step channels may open, with shifts to different current–voltage features over narrow voltage ranges.^{139–145} For example, in organized Langmuir–Blodgett donor–acceptor molecular films between a pair of metallic electrodes, the occupied donor level may initially be *lower* and the vacant acceptor level *higher* than the Fermi levels. The current flow is then insignificant when the electrode closest to the donor fragment is biased *positively*. If this electrode is biased, *negatively* current flow begins, however, when the donor level passes the acceptor level and the potential reverses the level positions (Figure 11). In this way, both rectification and switch effects can in principle be induced on the molecular scale. Such effects have been reported recently in the context of both solid-state^{146–147} quantum well structures composed of single- and multilevel Langmuir–Blodgett structures and in photoelectrochemical devices where current is induced by photoexcitation in assembled monolayers (electrochemical photodiodes).^{12,132} Environmental charge transfer control can thus impose composite and highly information dense current–voltage relations in structurally organized systems.

In comparison with the tunnel factor and driving force, the environmental reorganization Gibbs free energy has received less attention. Values of this quantity can be obtained from

free energy relations of intramolecular electron transfer which approach or traverse the activationless free energy range.^{121–124,148–151} They are also available from the current–voltage relations in electron transfer processes at organized self-assembled structures.^{129–131} In such anisotropic, often apolar systems the reorganization Gibbs free energy is, however, a composite molecular quantity^{87,152} and also assumes different values for electron transfer in different directions. The apolar nature of the immediate environment also calls for the need to consider details of the molecular charge distributions in the environment rather than bulk response functions such as the dielectric permittivity.¹⁵³

An intriguing tunneling effect was found recently in scanning tunneling microscopy (STM) and high-resolution transmission electron microscopy (TEM) studies of nanostructured palladium clusters covered with surfactants of variable carbon chain length.¹⁵⁴ It was found that TEM images the metal core of a cluster, but not the surfactant, whereas STM images the cluster with the surfactant tails. The fact that the STM in-plane images have larger radius than the pictures given by TEM may be an artifact in STM imaging due to the finite radius of the tip.¹⁵⁵ Since there is, however, an obvious correlation between the lateral size of the complex and the length of the surfactant tail, an artifact can be excluded in this case.¹⁵⁴ More important is that the surfactant seems to allow for high tunneling currents, practically as high as normal currents across the metal cluster. Whether this effect is due to resonance levels in the surfactant film or another reason is a question that could be answered by STM voltage spectroscopy.

Environmentally Controlled Organized Electron Transport in Metalloprotein Systems. Organized electron transport in biological systems is most commonly associated with individual metalloprotein molecules or larger metalloprotein complexes. The former are dominated by the small single-metal electron transport proteins cytochromes, blue copper proteins, and iron–sulphur proteins.^{34–36,38,156} The latter are multicenter protein complexes, such as the photosynthetic reaction centers,^{42,43} or redox enzyme complexes such as the cytochrome *c* oxidases^{39–41,157} and nitrogenases¹⁵⁸ where substrate oxidation and reduction occur at different protein sites connected by intramolecular electron transfer routes. As for synthetic molecular structures, environmental control of metalloprotein electron transport is of multifarious character and is reflected in all the rate parameters of the individual electron transfer steps. New features of coherent and cooperative electron transfer are, moreover apparent.

The theory of “organized” biological electron transport follows of course the same concepts and formalism as in synthetic molecular assemblies or mobile molecules. A number of new structural features are, however, particularly reflected in the electron transport patterns of biological systems.

a. Intermolecular Work Terms. Structural surface features for molecular recognition of reaction partners. The features can be geometric structural elements or distributions of charged amino acid residues. Cytochrome (cyt) *c* docking to cyt *c* oxidase,^{39,40} interaction of the plastocyanins (Figure 12)^{159–161} with cyt *f*^{162–164} or photosystem I,^{164,165} or the cyt *c*/*b*₅¹⁶⁶ and cyt *c*/cyt *c* peroxidase⁵⁰ complexes, are such examples. Docking is facilitated by the molecular size and is formally reflected directly in favorable interreactant work terms and, equally importantly but less directly, in the electronic tunnel factor.

b. Conformational Docking and Reorganization. Proteins are conformationally mobile. The mobility can assist docking by induced-fit interactions. The conformational system also constitutes an almost continuous distribution of low-frequency

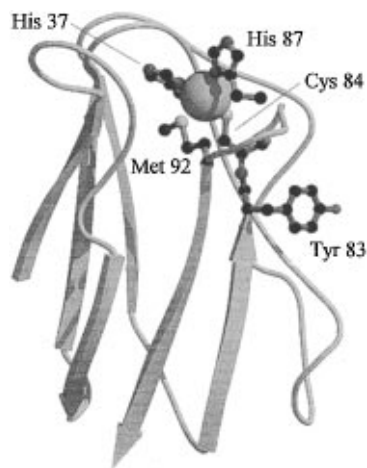


Figure 12. Three-dimensional structure of poplar plastocyanin. Coordinates are from ref 160 and the Brookhaven data bank.¹⁶¹ Graphics by the programme Molscript.¹⁵⁹ Critical residues in the two-electron transfer routes shown.

($\approx 100 \text{ cm}^{-1}$) dissipative nuclear modes^{167–169} reminiscent of the external solvent and is reorganized on charge transfer. Both electron transfer patterns in the photosynthetic reaction centers^{42,43,170,171} and free energy relations for electron transfer of individual metalloproteins such as cyt *c* or myoglobin^{36,172,173} show, moreover, that reorganization Gibbs free energies can be substantial (i.e., approaching one electron volt). The conformational system must therefore be incorporated in biological charge transfer formalism.

Incorporation on different levels is needed. Molecular features are sometimes reflected in multiexponential kinetics and in a hierarchy of relaxation times spanning many orders of magnitude. Prominent examples are the recombination reactions of carbon monoxide with myoglobins^{174–176} or nitrogen monoxide with azurin.¹⁷⁷ Such behavior formally emerges out of stochastic rate theory combined with multimode models which include both dissipative and friction-free motion.^{10,178–181} This framework has, however, a general character and models of a different kind must be added in order to endow specific molecular features. Molecular-level models can probably only be constructed by molecular dynamics simulation such as reported for example for superoxide dismutase,^{182,183} but much simpler views based on collective linear conformational modes or finite-boundary dielectric models^{184,185} are adequate in many cases where full vibrational equilibrium is ensured. In such cases conformational reorganization controls charge transfer in ways analogous to the solvent where details of the molecular motion can also be disregarded when vibrational equilibrium prevails.

In addition the aqueous medium imposes intriguing and highly non-trivial effects on the reorganization free energy and driving force. This is due to the location of most biological charge transfer centers near interfaces between the protein medium and the solvent, and they can be rationalized within the framework of classical electrostatic.²¹⁶ Nonlocal electrostatic theory has not been broadly applied to such problems but procedures are available and applied to interfacial dielectric system with simple interfacial geometries such as planar, cylindrical, and spherical.⁵⁹ Nonlocal electrostatics is known often to come up with counterintuitive predictions in interfacial problems⁵⁹ due to competition between the dielectric responses of the contacting phases. Application to biological charge transfer could thus hold promise, but little is here known about the true nonlocal response of the contacting system parts.

c. Electronic Tunnel Factor. One of the intriguing features of protein electron transport is that facile long-range electron transfer is either part of the natural biological function or can be brought to occur by chemical or biological protein modification.^{34–36,38–43,153,156,157,186} Distances can be over 15 Å in excess of the donor and acceptor centers, including the ligand groups. Metalloproteins therefore offer interesting probes for distance relations of the tunnel factor and the chemical nature of the environmental material between the donor and acceptor.

A common theoretical notion is the role of *intermediate* electronic states in addition to the donor and acceptor states.^{187–201} Combined with high-order perturbation theory such views give for the electron exchange factor

$$T_{\text{DA}} = V_{\text{DA}}^{(1)} + \sum_j^N V_{\text{DA}}^{(j)}$$

$$V_{\text{DA}}^{(j)} = \frac{V_{\text{D(B1)}}^{(1)} V_{\text{(B1)(B2)}}^{(1)} \dots V_{\text{(Bj)A}}^{(1)}}{(E_{\text{D}} - E_{\text{B1}})(E_{\text{D}} - E_{\text{B2}}) \dots (E_{\text{D}} - E_{\text{Bj}})} \quad (57)$$

$V_{\text{DA}}^{(1)}$ represents direct electron exchange between the donor (D) and acceptor (A) (usually unimportant). All other V -terms are interactions between the donor or acceptor, via the bridge groups characterized by the index Bj ($j = 1, \dots, N$). The denominators are the energy gaps between the states indicated by the subscripts, at the particular nuclear configuration where electron transfer occurs. Equation 57 states that the overall *amplitude* of the transition is a superposition of all routes involving any combination of bridge groups.

Views and formalism such as those inherent in eq 57 were introduced early in electron transfer theory.^{187–192} They prompt some observations: (A) the formalism applies in the *perturbation* limit (i.e., when $V_{\text{ST}}^{(1)} \ll E_{\text{D}} - E_{\text{Bj}}$ ($S, T = \text{D, A, Bj}$)). The choice of basis set therefore needs care. LCAO MOs of individual residues, for example,²⁰¹ comfortably meet this condition whereas the adequacy of commonly used atomic basis sets are in need of substantiation. (B) If all $V_{\text{(Bj)(Bj+1)}}^{(1)} = \beta$, all energy gaps $E_{\text{D}} - E_{\text{Bj}} = \Delta$, $V_{\text{D(B1)}}^{(1)} = \beta_{\text{D}}$ and $V_{\text{(Bj)A}}^{(1)} = \beta_{\text{A}}$ then the term of highest order ($j = N$) in eq 57 dominates and T_{DA} reduces to the form²⁰².

$$T_{\text{DA}} \approx (\beta_{\text{D}} \beta_{\text{A}} / \beta) \exp \{-(R/a) \ln(\Delta/\beta)\} \quad (58)$$

where a is the average bridge group extension and R the donor–acceptor distance *along the direction* spanned by the bridge groups. This equation shows that the larger the energy gap and the poorer the overlap the faster the electronic coupling falls off.

Views based on eqs 57 and 58 are basis for recent broad application of simple “pathway” considerations in electron transfer along the backbones or through hydrogen bond and space links in metalloproteins.^{35,197,198} In practical use the quantity β/Δ is assigned some value (< 1) and the mere *number* of links between the donor and acceptor in a given route taken as the determining factor in the donor–bridge–acceptor coupling. Figure 13^{159,161,203,204} shows such a putative dominating route for intramolecular electron transfer between the pulse radiolysis generated disulphide anion radical in one end of the azurin molecule to the copper atom in the other end.²⁰⁴ While crude, the simple bond-counting views are useful in selecting protein fragments for which proper calculations are warranted. They can also help towards the illustration of functional principles for metalloproteins. The plant plastocyanins illustrate this (Figure 12). *Two* dominating electron transfer routes in these single-copper proteins can be identified.^{163,201,205} One is

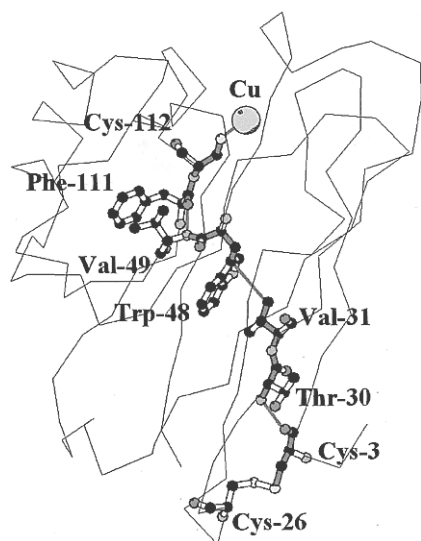


Figure 13. Three-dimensional structure of *Pseudomonas aeruginosa* azurin. Coordinates are from ref 203 and the Brookhaven data bank.⁶¹ Graphics by the programme Molscript.¹⁵⁹ A putative electron transfer route from the Cys3Cys26 disulfide bridge to the copper atom through the protein is shown, as suggested in ref 204.

near the copper atom and involves a single residue only (His87). The other one is via Cys84/Tyr83. This spatially longer route is electronically about two orders of magnitude less facile due to the additional intermediate residue. The route is, however, assisted by negatively charged surface residues around Tyr83. Favorable electrostatic interactions toward positively charged reaction partners overcome the less facile electronic coupling and make this route competitive. This molecule is therefore representative of an interesting feature of “organized” biological electron transport, resting on a subtle balance between intermolecular recognition (work terms) and electronic properties (the electronic factor), endowing the electron transport with directional functionality.

Some limitations restrict the use of this simple palatable approach: (C) Equations 57 and 58 in the form shown fail as $\Delta \rightarrow 0$. This occurs when low-lying intermediate states are located along the electron transfer routes. Tunnel barrier fluctuations or temporary level population are then important and the fundamental nature of the tunnel process different. This is considered below. Electron transfer initiated by photoexcitation may approach such conditions where use of eqs 57 and 58 needs reconsideration.

(D) In long-range limits the electronic factor can in principle depend strongly on the nuclear fluctuations, and the Condon approximation even fail.^{33,206–208} Investigations of self-consistent electronic–vibrational interaction based on analytical models have shown both that electron tunnelling is then strongly facilitated at the non-equilibrium environmental configuration and that a notably smaller activation Gibbs free energy emerges.^{33,207} The effects are obviously smaller in cavity models where the repolarization is smaller.⁸⁷ All the many interesting reported cases of photoinitiated biological electron transfer therefore offer cases for investigating also *subtler* effects of organized molecular electron transport.

d. Coherent and Cooperative Electron Transfer. Electron transport networks in multicenter systems display elements of cooperativity of physically different form. In cases where the processes are slow enough that conformational relaxation is fully established after each step, the single-electron transfer formalism applies. “Cooperativity” here implies that the thermodynamic and electronic properties of a given center are changed when electron transfer between other centers occurs. Such effects can

be dominated by electrostatics or transmitted by the conformational system. An example of the former is the electron transfer pattern of the bacterial di-heme protein cytochrome *c*₄.²⁰⁹ Partly conformationally transmitted cooperative multielectron transfer is represented by the four-heme cytochromes *c*₃.^{45,46}

A rather different kind of environmentally controlled multielectron transfer cooperativity follows from the superexchange modes represented by eq 57. As $\Delta \rightarrow 0$ and intermediate states traverse the donor–acceptor potential surface crossing, these states become temporarily populated. Formal inclusion of the continuous vibrational dispersion in *all* the states is now essential,^{189–194,200} and simple use of eq 57 fails. A variety of new physical features then emerges. These are discussed in detail elsewhere,^{194,200} but we note the following in the context of the present discussion: (1) The continuous vibrational manifold ensures that the formal divergence in eq 57 as $\Delta \rightarrow 0$ is replaced by a finite mild resonance. This is equivalent to resonance Raman scattering and other three-level electronic processes in condensed media.^{194,200}

(2) The quantum mechanical three-level electronic transition has a rate constant of the form

$$W_{DA} \sim \gamma_{BD}\gamma_{AB} \exp(-G_{ABD}^{\ddagger}/k_B T) \quad (59)$$

where G_{ABD}^{\ddagger} is the activation (Gibbs free) energy while γ_{BD} and γ_{AB} are the Landau–Zener factors at the $D \rightarrow B$ and $B \rightarrow A$ crossing, respectively. Coherence between the two transitions is apparent by the presence of *two* electronic factors in the preexponential factor. Two fully relaxed single-electron transfers would only hold the electronic factor of the slower step. This points to the vibrationally unrelaxed nature of the intermediate state, and the single-passage character of the transition.

(3) Vibrational relaxation in the intermediate state must be incorporated explicitly. This is feasible by specific damping features or separate vibrational relaxation channels.^{135,200} In these ways the whole range from purely coherent quantum mechanical two-step behavior to fully vibrationally relaxed stepwise single-electron transfer is covered.

The formalism of coherent electron transfer holds perspectives for fast chemical and biological electron transfer networks. One of the most conspicuous targets would be the primary, subpicosecond charge separation in the bacterial photosynthetic reaction centers involving special pair and auxiliary chlorophylls and pheophytin.⁴³ Other, synthetic three-center charge transfer systems rest on linked porphyrin/quinone systems.^{121,150} Environmentally controlled organized electron transfer acquires new perspectives in relation to these systems.

Conclusions and Outlook

The overarching object of the discussion above is to approach the multifarious roles of the reaction medium in physical, chemical, and biological charge transfer. Once the variability of static and dynamic environmental effects has been identified, incorporation of these effects in the elementary rate constants can be achieved by combining the general formalism of solution chemical rate theory with suitable *models*. Crucial differences between charge transfer in physical, chemical, and structurally “organized” media can subsequently be disentangled. The following static and dynamic environmental effects can be identified in the overall scenario of even the simplest charge transfer process: (A) The donor and acceptor centers are *in general* initially infinitely remote from one another, with widely different equilibrium donor and acceptor electronic energies. The former may be unimportant in intramolecular electron

transfer whereas the latter *always* applies. The first crucial role of the environment is therefore to provide a medium for Brownian reactant motion toward suitable relative orientation and long enough residence time for charge transfer to occur. Both diffusional barriers and interreactant forces are involved in this stage.

(B) The environment imposes distortion on the *equilibrium* structural and thermodynamic reactant and product properties, determined by the dielectric and other characteristics of the environment and by the electronic properties of the isolated reactant and product molecules. A pragmatic consequence is that the reaction Gibbs free energy (driving force) is controlled by the solvation forces.

(C) Once a "precursor" complex is formed, environmental *dynamics* impose donor and acceptor level broadening. This feature constitutes both important contributions to the overall activation Gibbs free energy and ensures level matching crucial in the radiationless character of the transition. The instantaneous level energy is thus "distributed" with decisive implications for the character of the multiphonon liquid or solid state charge transfer process.

(D) The *continuous* level distribution is central in other respects. In the *adiabatic* limit and Fermi Golden Rule concepts it ensures process irreversibility. In the *adiabatic* limit environmental nuclear multidimensionality ensures process irreversibility by energy dissipation and dephasing, as well as by product molecule diffusion out of the reaction zone.

(E) Environmental matter can fill the space between the donor and acceptor centers. A variety of environmental effects on the electron exchange factor then arises. These relate to the nonequilibrium nature of the perturbation inducing the transition and to fluctuational effects on the electronic wave functions at the moment of electron transfer.

Charge transfer theory in principle incorporates *all* these environmental effects and their different importance in liquid and solid media. The outcome is, however, rather system specific, and the different functions are interconnected. For example, freezing of given nuclear modes is not a panacea for rate increase, and complete freezing simply blocks the functions (C) and (D). The rate theory here provides prescriptions for characterizing the optimum conditions.

Contemporary charge transfer theory offers a comprehensive overarching frame for the multifarious patterns of numerous individual cases in physics, chemistry, and biology and has in this sense evolved to something resembling a major general *law* in chemistry. Charge transfer theory offers approaches to the determining factors of chemical and biological processes including precise ways of incorporating the environment. Crucial in such contexts is, for example, the different reflection of the environmental effects in liquid- and solid-state processes, as are ways in which biological and synthetic ordered supramolecular systems compare with the more conventional liquid and solid-state environments.

Environmental effects are frequently straightforward and in line with intuitive expectations. For example, the reorganization Gibbs free energy is the most central determining environmental quantity in simple, approximately thermoneutral processes, and rate constant trends here follow those of the reorganization free energy. General correlations are therefore most easily recognized for this class. For example, 1. The response of the medium to the electric field aroused by the reactants is determined by the force constants of the vibrational modes (i.e., their frequencies). The more "rigid" the medium structure (the higher the frequencies), the lower the reorganization energy. Such a conclusion is straightforward when it applies to the

discrete local modes or underdamped vibrations in the medium (phonons). 2. The dielectric response function is the more appropriate characteristic for disordered and liquid polar media. In the simplest case this function is characterized largely by the optical and static dielectric constants, and the smaller the response (in the simplest case, the static dielectric constant), the lower is the reorganization free energy. Symmetric (thermoneutral) reactions therefore proceed faster in less polar media with a more rigid structure. In this respect, at all other conditions equal, solids may provide a better environment for a reaction than a polar liquid. The spatial dispersion may reinforce this tendency: in liquids it enhances the integral response, while in crystals with the Lorentzian form of spatial dispersion it depresses the response. 3. The effects of the ionic atmosphere are similar in liquid and solid electrolytes and always increase the activation barrier (a nontrivial conclusion, since the ionic atmosphere screens the static field of the reactants). However, for strongly polar media, as in aqueous electrolytes, the effect is negligible, while for low-polar media, such as in solid electrolytes, it may reach several orders of magnitude in the rate constant.

For nonsymmetric reactions charge recombination and charge separation should be distinguished and attention given not only to the reorganization free energy, but also to the reaction free energy. In particular, 1. As for thermoneutral reactions, the activation Gibbs free energy of recombination in the *normal region* (where the symmetry factor is between zero and unity), decreases as the dielectric constant is lowered, whereas it increases in the inverted region. Normal recombination reactions would thus run faster in solids than in polar liquids, while this is *opposite in the inverted region*. 2. The activation free energy for charge separation increases with the decrease of the dielectric constant in both regions. Such reactions in solids would therefore be slower than in polar liquids.

An additional environmentally rooted quantity is the contribution to the activation free energy from the electrostatic repulsion or attraction between mobile charged species, when the interreactant distance is not fixed. How large is this contribution? Calculations based on classical electrostatics give relatively small values, but this may be different when nonlocal effects are incorporated. The latter are very sensitive to the size and the smearing of the reactant charge distribution. Conclusions regarding this effect can be drawn for case studies. However, the Debye screening reduces the interaction and this dominates over all other ionic atmosphere effects. (Reactions between the like-charged ions are known to be faster, the more concentrated the solution.)

Can we say something general about the role of the medium in the preexponential factor? Hardly anything about the electronic matrix element in diabatic reactions, which depends on the detailed structure of the reactants and their short-range environment. For adiabatic reactions in media with overdamped modes, the preexponential is inversely proportional to the effective relaxation time. In media with larger microscopic viscosity, the preexponential factor is therefore smaller, but a priori comparison of liquids and solids would be hard. If there are several reactive modes, the effective relaxation time is determined by the mode with the largest reorganization free energy and the smallest relaxation time.

Charge transfer theory finally extends to the special structures and electronic properties of organized supramolecular assemblies and of biological electron transport. Much focus so far has been on mildly committing notions such as driving force effects and long-range electron transfer on which simple views such as bond-counting concepts have been overduely imposed. At the

same time, exactly these systems offer much wider perspectives for illumination of subtler effects of considerable importance as indicated by theoretical analysis. Fluctuational tunneling, self-consistent electronic—vibrational interaction, and coherent multielectron transfer were noted above. Efforts in these areas can be extended for example to preciser electronic structure representations, multidimensional nuclear (dissipative and friction-free) motion, and to electronic level broadening in organized two-dimensional Langmuir—Blodgett-like donor—acceptor structures. Multilevel electron transfer formalism can also be bridged to other molecular processes such as Raman and resonance Raman spectroscopy,^{135,200,210} coherent anti-Stokes Raman scattering,²¹¹ scanning tunnel microscopy^{135,136,212} (STM) and, in longer terms, higher order processes such as second-harmonic generation and other nonlinear processes. Other areas where efforts in charge transfer theory can be envisaged relate either to new *phenomena* or to new approaches to recognized features. The former are for example electronic tunnelling and surface charge density lability in electrochemistry and in situ STM processes,²¹³ and charge transfer near phase transitions,^{214,215} with interesting perspectives for phase transfer catalysis and biological membrane control. The latter would be directed for example to anisotropic environmental nuclear reorganization, molecular charge distributions in polar and apolar environments, and conformational relaxation in protein systems.

Charge transfer theory is also becoming a most powerful tool in experimental chemistry. This extends *both* to all the subtle effects representative of physical and chemical reality *and* to new intriguing areas in molecular physics and chemistry. In this respect the use of charge transfer laws is almost coming to resemble the way that theoretical manybody concepts have become powerful tools in experimental physics.

Acknowledgment. Thanks are due to Volkswagen Stiftung which made this work possible through partial support by Grant I 69529. Financial support from the Danish Natural and Technical Science Research Councils, the EU INTAS Program, and the Carlsberg and Novo Nordisk Foundations is also gratefully acknowledged. We wish to thank Mr. E. P. Friis and Mr. P. Joecken for their help in preparation of figures.

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