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The new theory of electron transfer. Thermodynamic potential profiles in the inverted and superverted regions

Stephen Fletcher

Abstract In a previous paper (S Fletcher, *J Solid State Electrochem* 11:965, 2007) a non-Marcus theory of electron transfer was developed, with results applicable to the normal region of thermodynamic driving forces. In the present paper, the theory is extended to highly exergonic reactions (the inverted region) and to highly endergonic reactions (the superverted region). The results are presented mathematically and in the form of Gibbs energy profiles plotted against a charge fluctuation reaction coordinate. The new theory utilizes the concept of donor and acceptor "supermolecules," which consist of conventional donor and acceptor species plus their associated ionic atmospheres. The key findings are as follows. (1) In the inverted region, donor supermolecules are positively charged both before and after the electron transfer event. (2) In the normal region, donor supermolecules change polarity from negative to positive during the electron transfer event. (3) In the superverted region, the donor supermolecule is negatively charged both before and after the electron transfer event. This overall pattern of events makes it possible for polar solvents to catalyse electron transfer in the inverted and superverted regions. Because this new effect is predicted only by the present theory and not by the Marcus theory, it provides a clear means of distinguishing between them.

Keywords Marcus theory · Electron transfer theory · Reorganization energy · Inverted region · Superverted region · Exergonic reactions

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Introduction

In general, three conditions must be met before electron transfer can occur between two species in solution. These are (1) the Conservation of Energy, (2) the Franck–Condon Principle and the (3) Principle of Microscopic Reversibility [1–3]. In addition, the surrounding heat bath must supply enough energy to create the transition states of the donor and acceptor. In the present work, we are concerned with elucidating the mechanism of the latter process.

A possible mechanism was conjectured by Marcus in 1956 [4] and elaborated in a number of follow-up papers [5–10]. According to Marcus, electron transfer is driven by fluctuations in the dielectric constant of the solvent in the vicinity of the donor and acceptor species. Marcus calls these "solvent fluctuations." They allow the donor and acceptor species to equalize their energies many millions of times per second, on each occasion providing an opportunity for electron tunnelling to occur. Today, this simple and appealing idea underpins the entire field of electron transfer.

However, is it right? To function according to the Marcus scheme, the dielectric fluctuations must have charge fluctuations on which to act, yet the work needed to form the charge fluctuations is missing from the theory. Recent analysis has proved this [3] and has also shown that the omission causes the equation for the reorganization energy to diverge in the limit of non-polar solvents. As we shall now demonstrate, the same problem also leads to unphysical predictions at extreme driving forces. Summarizing the current situation, we feel confident in asserting that the Marcus theory neglects the work to form charge fluctuations and considers only the work to un-screen them.

To overcome this difficulty, I recently proposed a non-Marcus model of electron transfer in which energy equalization between reactants and products is achieved
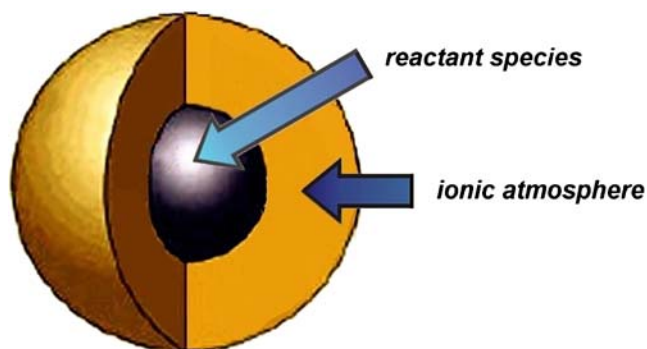
Fig. 1 The concept of a "supermolecule"

by charge fluctuations in the ionic atmospheres of the donor and acceptor species, rather than by dielectric fluctuations [3]. The donor and acceptor species, plus their ionic atmospheres, are treated as "supermolecules," which are electroneutral in the time-averaged sense but subject to charge fluctuations in real time. The concept of a supermolecule is shown in Fig. 1. Its radius is the Debye length, λ_D, which is just the average distance needed for screening the permanent charge on the reactant species.

In the outer regions of the supermolecule, charge fluctuations are occurring continually by the random thermal motion (Brownian motion) of co-ions, counter-ions and solvent dipoles. In particular, charge fluctuations are continually being injected into (and extracted from) the supermolecule by the bulk of the solution.

In the present paper, equations are derived for the shape of the thermodynamic potential energy profiles of the reactant and product sub-systems across the whole range of driving force ($-\Delta G^0$), and some consequences of this new model are explored. Remarkably, the new model predicts that the rate constant is a piecewise function of the driving force, with different definitions over different intervals. This is in sharp contrast with the Marcus theory,

which predicts that the rate constant is a single function of driving force. The difference should be amenable to experimental testing.

Results

Figure 2 shows the thermodynamic potential profiles of reactant and product sub-systems during electron transfer, plotted as a function of the charge fluctuation on the donor supermolecule, in the "normal" region of driving force $-\lambda < \Delta G^0 < \lambda$.

As far as mathematical modelling is concerned, some choice is available regarding the selection of the thermodynamic variable. However, we have chosen to work with the Gibbs potential because the electron transfer reaction is assumed to take place inside a heat bath at constant mean temperature, pressure and electrostatic potential. No choice is available regarding the reaction co-ordinate. Throughout the present work, the charge fluctuation on the donor (or, equivalently, the acceptor) is the only possible reaction co-ordinate because no other kind of activation process is considered (far from being inconvenient, this actually turns out to be highly convenient because charge is an independent degree of freedom of the system, and so its Gibbs potential profile is always a parabola). Given our choice of axes, the only free parameters left in the system are ΔG^0 and λ. The parameter ΔG^0 is the total Gibbs energy change of the reaction, so that $-\Delta G^0$ may be regarded as the thermodynamic "driving force." The parameter λ is commonly referred to as the "reorganization energy," although—strictly speaking—it is actually a measure of the total work that the external world must do on the combined donor and acceptor species to excite them into their transition states.
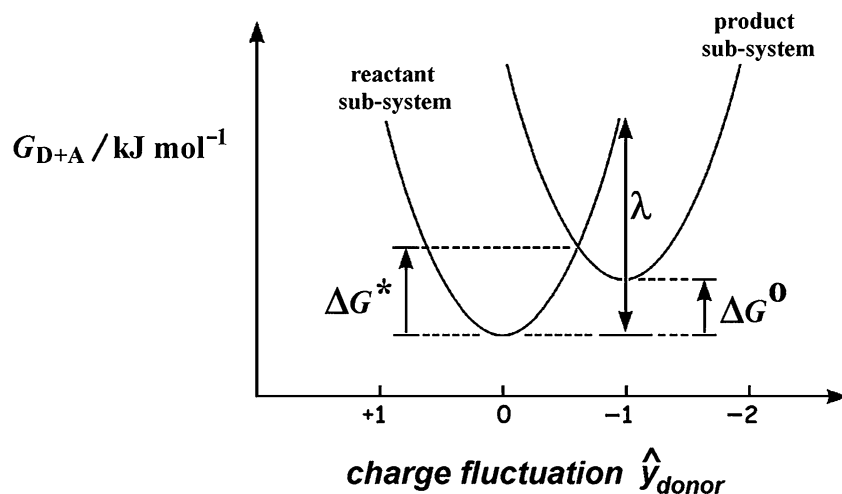

Fig. 2 Thermodynamic potential profiles of reactant and product sub-systems during electron transfer, plotted as a function of the charge fluctuation on the donor supermolecule, in the "normal" region of driving force $-\lambda < \Delta G^0 < \lambda$

On the Marcus theory, the reaction co-ordinate is a complex parameter related to the positions of hundreds of local solvent molecules surrounding the donor and acceptor [10]. On the Fletcher model [3], the reaction co-ordinate is much simpler. It is just the fluctuation of charge number $\hat{y}$ on the donor supermolecule:

$$\hat{y}_{donor} = y_{donor} - \langle y_{donor} \rangle$$

In this equation, terms inside circumflex brackets are time-averaged quantities, and terms outside circumflex brackets are instantaneous values. Because charge fluctuations at thermodynamic equilibrium are ergodic, it follows that the bottom of the parabola corresponds to electroneutrality of the supermolecule (this observation also serves to remind us that the condition of electroneutrality is valid only on spatial and temporal average and that local fluctuations of charge nevertheless occur everywhere throughout electrolyte solutions).

At this point, we should like to emphasize that the parabolic shape of the Gibbs potential profile is not a feature unique to Marcus theory. In fact, it has been known since the time of Langevin that for small fluctuations about local equilibrium, the Gibbs energy has a parabolic dependence on every degree of freedom of the system. As a result, the experimental observation of parabolic potential profiles is not sufficient to validate the Marcus theory. Even more importantly, the observation of an experimental "inverted region" is not sufficient to validate the Marcus theory either. Most theories of electron transfer (including my own [3]) also predict an inverted region, although with possibly different properties compared with the Marcus approach.

In Fig. 3, we identify three different regions of electron transfer within the new model, which we have labeled the "inverted region," the "normal region" and the "super-verted" region. The first two labels are conventional; the third is new. The regions are defined mathematically, as follows:

- "Inverted region" $(\Delta G^0 < -\lambda)$
- "Normal region" $(-\lambda < \Delta G^0 < \lambda)$
- "Superverted region" $(\Delta G^0 > \lambda)$

It is interesting to note that when the Gibbs energies of the reactant and product sub-systems (the combined energies of the "supermolecules") are plotted against the charge fluctuation reaction co-ordinate $\hat{y}$, we see immediately that the different branches of the parabolas correspond to different polarities of the reactant and product supermolecules (Fig. 3).

For the donor supermolecules, the left-hand branches are positive, and the right-hand branches are negative (the converse is true for the acceptor supermolecules). As a result, there are three fundamentally different types of transition that may occur during electron transfer. In the inverted region, the
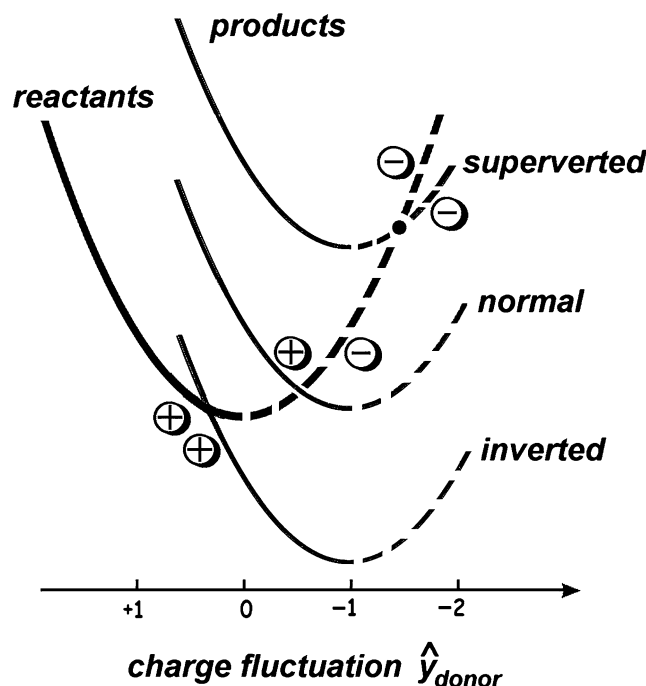

Fig. 3 The three regions of electron transfer, in the case of a non-polar solvent. The *solid lines* indicate where the donor supermolecule is positively charged. The *dashed lines* indicate where the donor supermolecule is negatively charged

donor supermolecule is positively charged both before and after the electron transfer event. In the normal region, the donor supermolecule changes polarity from negative to positive during the electron transfer event. Finally, in the superverted region, the donor supermolecule is negatively charged both before and after the electron transfer event (the reverse pattern is true for the acceptor supermolecules).

Because the polarities of the supermolecules do not change during charge transfer in the inverted and the superverted regions, some degree of solvent stabilization (i.e. some degree of bulk solvent orientation towards the supermolecules) is allowed in both cases, without violating the principle of microscopic reversibility. However, in the normal region, orientated solvent molecules are strictly excluded from the transition state because they would be required to reverse direction instantaneously at the moment of electron transfer.

Figure 4 shows how polar solvent screening catalyses electron transfer in the inverted region, as compared with the unscreened situation. The polar solvent molecules are attracted to the charge fluctuations in the transition state, thus lowering the activation energy of the reaction. The activation energy is lowered from T_1 to T_2, and so the rate of reaction is speeded up. Given that the positive charge on the donor supermolecule actually increases by one unit as a result of electron transfer in this region, the orientation of the solvent dipoles is not "wrong," and their persistence into the product state does not violate microscopic reversibility.
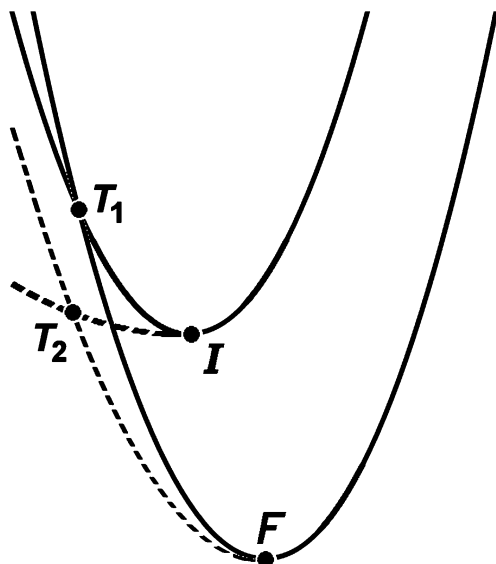
Fig. 4 The behaviour of potential energy profiles in the inverted region. *Solid lines* indicate the system behaviour in non-polar solvents or in the absence of polar solvent screening. *Dotted lines* indicate solvent-stabilized states. *I* Initial state of the system, *F* final state of the system. T_1 is the transition state in a non-polar solvent. T_2 is the transition state in a polar solvent

Analogous logic applies in the superverted region (Fig. 5). Once again, the polar solvent molecules are attracted to the charge fluctuations in the transition state, thus lowering the activation energy of the reaction. The activation energy is lowered from T_3 to T_4, and so the rate of reaction is speeded up. This time, however, the negative
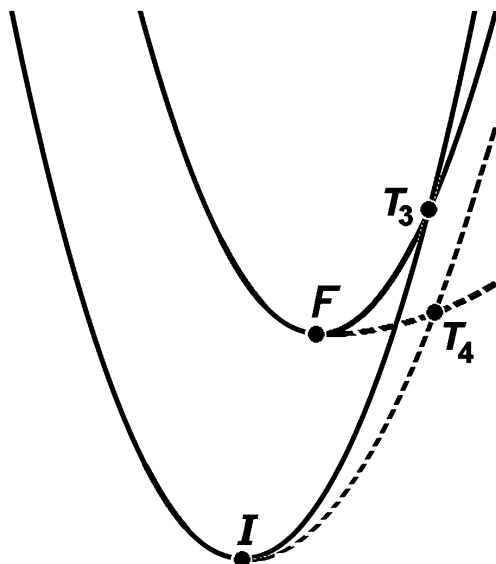

Fig. 5 The behaviour of potential energy profiles in the superverted region. *Solid lines* indicate the system behaviour in non-polar solvents or in the absence of polar solvent screening. *Dotted lines* indicate solvent-stabilized states. *I* Initial state of the system, *F* final state of the system. T_3 is the transition state in a non-polar solvent. T_4 is the transition state in a polar solvent

charge diminishes by one unit during electron transfer, so only a fraction of the total possible screening is permitted by microscopic reversibility.

Completing the analysis, in the normal region, screening by polar solvent molecules in the transition state is forbidden by microscopic reversibility.

Analytical solutions

(1) The inverted region:

In an ideal non-polar solvent,

$$G_{reactants} = \frac{1}{2} Q_1^2 \left(\frac{1}{4\pi\varepsilon_0} \right) \left(\frac{1}{\varepsilon_{(\infty)}} \right) \left(\frac{1}{a_D} + \frac{1}{a_A} - \frac{2}{d} \right)$$

$$G_{products} = \frac{1}{2} Q_2^2 \left(\frac{1}{4\pi\varepsilon_0} \right) \left(\frac{1}{\varepsilon_{(\infty)}} \right) \left(\frac{1}{a_D} + \frac{1}{a_A} - \frac{2}{d} \right)$$

In a polar solvent,

$$G_{reactants} = \frac{1}{2} Q_1^2 \left(\frac{1}{4\pi\varepsilon_0} \right) \left(\frac{1}{\varepsilon_{(0)}} \right) \left(\frac{1}{a_D} + \frac{1}{a_A} - \frac{2}{d} \right)$$

(e.g. for water, about 40× smaller than the non-polar case!)

$$G_{products} = \frac{1}{2} Q_2^2 \left(\frac{1}{4\pi\varepsilon_0} \right) \left(\frac{1}{\varepsilon_{(\infty)} + f_1 \left[\varepsilon_{(0)} - \varepsilon_{(\infty)} \right]} \right) \left(\frac{1}{a_D} + \frac{1}{a_A} - \frac{2}{d} \right)$$

where f_1 is a constant such that $0 < f_1 < 1$. On a linear model,

$$f_1 \approx \frac{\beta}{\beta + 1}$$

Therefore, for $\beta = 1/2, f_1 \approx 1/3$

(2) In the normal region:

In both polar and non-polar solvents,

$$G_{reactants} = \frac{1}{2} Q_1^2 \left(\frac{1}{4\pi\varepsilon_0} \right) \left(\frac{1}{\varepsilon_{(\infty)}} \right) \left(\frac{1}{a_D} + \frac{1}{a_A} - \frac{2}{d} \right)$$

$$G_{products} = \frac{1}{2} Q_2^2 \left(\frac{1}{4\pi\varepsilon_0} \right) \left(\frac{1}{\varepsilon_{(\infty)}} \right) \left(\frac{1}{a_D} + \frac{1}{a_A} - \frac{2}{d} \right)$$

(3) In the superverted region:

In an ideal non-polar solvent,

$$G_{reactants} = \frac{1}{2} Q_1^2 \left(\frac{1}{4\pi\varepsilon_0} \right) \left(\frac{1}{\varepsilon_{(\infty)}} \right) \left(\frac{1}{a_D} + \frac{1}{a_A} - \frac{2}{d} \right)$$
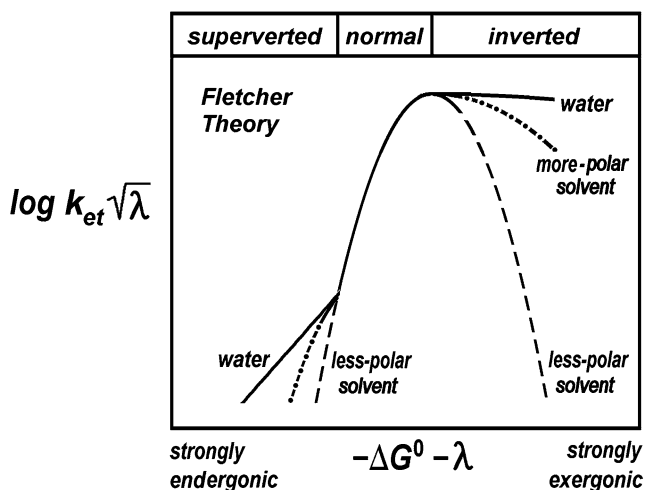
Fig. 6 Schematic diagram showing how the rate constant for electron transfer (k_{et}) varies with driving force ($-\Delta G^0$) on the Fletcher theory [3]

$$G_{products} = \frac{1}{2} Q_2^2 \left(\frac{1}{4\pi\varepsilon_0}\right) \left(\frac{1}{\varepsilon_{(\infty)}}\right) \left(\frac{1}{a_D} + \frac{1}{a_A} - \frac{2}{d}\right)$$

In a polar solvent,

$$G_{reactants} = \frac{1}{2} Q_1^2 \left(\frac{1}{4\pi\varepsilon_0}\right) \left(\frac{1}{\varepsilon_{(\infty)} + f_2 \left[\varepsilon_{(0)} - \varepsilon_{(\infty)}\right]}\right) \left(\frac{1}{a_D} + \frac{1}{a_A} - \frac{2}{d}\right)$$

$$G_{products} = \frac{1}{2} Q_2^2 \left(\frac{1}{4\pi\varepsilon_0}\right) \left(\frac{1}{\varepsilon_{(0)}}\right) \left(\frac{1}{a_D} + \frac{1}{a_A} - \frac{2}{d}\right)$$

where f_2 is a constant such that $0 < f_2 < 1$.

The interplay of all of the above equations on the rate constant for electron transfer is summarized schematically
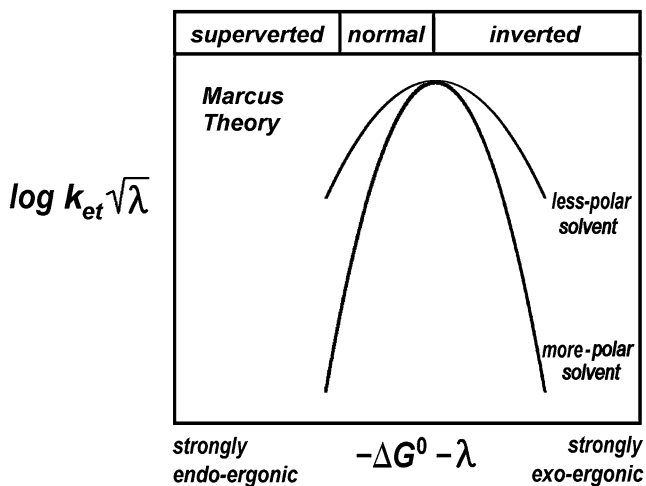

Fig. 7 Schematic diagram showing how the rate constant for electron transfer (k_{et}) varies with driving force ($-\Delta G^0$) on the Marcus theory [4–10]

in Fig. 6, assuming long-range (non-adiabatic) electron transfer according to Dirac's "golden rule" formulation [11]

$$k_{et} = \frac{2\pi}{\hbar} H_{DA}^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(\lambda + \Delta G^0)^2}{4\lambda k_B T}\right)$$

In this equation, k_{et} is the rate constant for electron transfer, H_{DA} is the electronic coupling between the donor and acceptor supermolecules, k_B is the Boltzmann constant, λ is the reorganization energy, and ΔG^0 is the total Gibbs energy change for the reaction.

It is clear that the rate constant for electron transfer is actually a piecewise function, comprising sections of different parabolas, extending across different domains of driving force ($-\Delta G^0$). The reason for this fragmentation is simply that the electron transfer reaction is catalysed by polar solvents in the inverted and superverted regions but is not catalysed in the normal region. As mentioned above, all that is needed for catalysis by polar solvents is for the sign of the charge fluctuations in the transition states of the supermolecules to be the same immediately before and immediately after electron transfer. We therefore predict catalysis by polar solvents to be a widespread phenomenon in nature. Furthermore, because this type of catalysis relies upon the electrostatic attraction of solvent molecules towards the transition state, we expect that there should be a negative contribution to the entropy of activation (and a negative contribution to the volume of activation) associated with the effect.
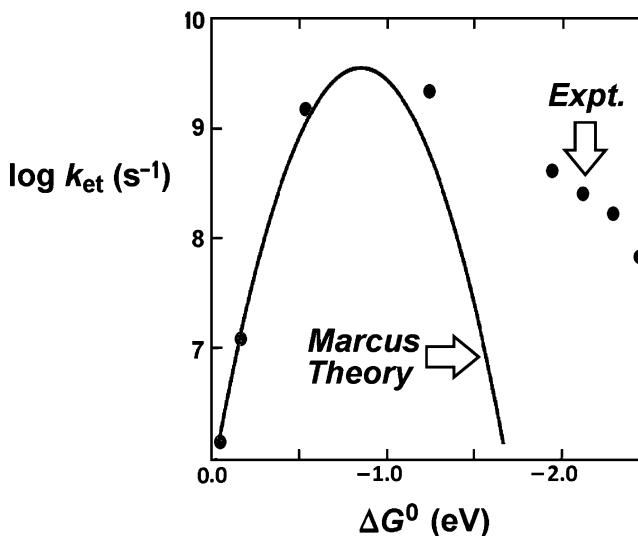

Fig. 8 Experimental electron transfer rate constants as a function of the total Gibbs energy change. Data redrawn from Miller et al. [12]. Electrons transferred intra-molecularly from a bi-phenyl donor group to eight different acceptor groups, in 2-methyl tetrahydrofuran at 296 K. The solvent dielectric constant was 6.97 (data obtained by a pulse radiolysis technique)

It is interesting to compare the above results with the predictions of the Marcus theory. The relevant equations are

$$G_{reactants} = \frac{1}{2} Q_1^2 \left(\frac{1}{4\pi\varepsilon_0}\right) \left(\frac{1}{\varepsilon_{(\infty)}} - \frac{1}{\varepsilon_{(0)}}\right) \left(\frac{1}{a_D} + \frac{1}{a_A} - \frac{2}{d}\right)$$

$$G_{products} = \frac{1}{2} Q_2^2 \left(\frac{1}{4\pi\varepsilon_0}\right) \left(\frac{1}{\varepsilon_{(\infty)}} - \frac{1}{\varepsilon_{(0)}}\right) \left(\frac{1}{a_D} + \frac{1}{a_A} - \frac{2}{d}\right)$$

and the corresponding behavior of the rate constants for electron transfer is summarized schematically in Fig. 7. On the Marcus theory, single-symmetric parabolas appear across the whole domain of $-\Delta G^0$. Furthermore, on the Marcus theory, polar solvents are predicted to act as inhibitors (not catalysts) of the electron transfer reaction. These significant differences between the Marcus theory and the present theory should be amenable to experimental study.

Conclusion

One of the historic goals of electron transfer theory has been to elucidate the mechanism by which ambient media are able to supply enough energy to create the transition states of the donor and acceptor species. In a previous paper, we postulated that for electrolyte solutions, this mechanism was one of charge fluctuations that are introduced into the ionic atmospheres of the reactants by the random motion of co-ions, counter-ions, and solvent dipoles [3]. In the present work, we have extended the theory to extreme values of driving force. The results are sketched in Fig. 6, which illustrates how the rate constants for electron transfer (k_{et}) vary with the driving force ($-\Delta G^0$). The graphs differ profoundly from those predicted by the Marcus theory (Fig. 7). One of the most striking differences is that the rate constants typically have a steeper slope in the normal region than in the inverted region. On the Marcus theory, the corresponding plot is always symmetric.

To decide which theory is better—the Marcus theory or the present theory—it will be necessary to acquire experimental data at high driving forces. Unfortunately, it is notoriously difficult to obtain such data because of the finite waiting time for donors and acceptors to diffuse together. However, Miller et al. [12] have already shown that it is possible to avoid this problem, by tethering donors and acceptors together inside bi-functional molecules. Their principal results are shown in Fig. 8. It is clear that the experimental data of Miller et al. are inconsistent with the Marcus theory. Furthermore, the experimental data are fully consistent with the theory proposed in the present work.

A second major difference between the Marcus theory and the Fletcher theory is the effect of the dielectric constant of the solvent on the rates of highly exergonic reactions. In the inverted region, on the Marcus theory, the rate constants for electron transfer are predicted to increase in less polar solvents, whereas on the Fletcher theory, the rate constants are predicted to decrease in less polar solvents. It is interesting to note that Miller et al. [12] also reported some data in a less polar solvent namely, isooctane ($\varepsilon_{(0)}=1.94$). Compared with the more polar solvent 2-methyl tetrahydrofuran ($\varepsilon_{(0)}=6.97$), their experimentally determined rate constants decreased by factors as large as 60. Once again, their results are inconsistent with the Marcus theory and consistent with the present theory, although more extensive data sets will clearly be needed to settle the issue.

Appendix: List of symbols

a_A	the radius of the acceptor supermolecule in the transition state
a_D	the radius of the donor supermolecule in the transition state
d	the centre-to-centre distance between D and A
$-e$	Charge on the electron
ε_0	the permittivity of free space
$\varepsilon_{(0)}$	the relative permittivity (dielectric constant) of the solution in the low frequency limit
$\varepsilon_{(\infty)}$	the relative permittivity (dielectric constant) of the solution in the high frequency limit
f_1, f_2	constants that quantify the extent of polar screening
ΔG^0	the total Gibbs energy change of the reaction
H_{DA}	electronic coupling matrix element
k_{et}	the rate constant for electron transfer
λ	the reorganization energy of the reaction
Q_1	charge fluctuation on a donor supermolecule
y	charge number on a donor supermolecule

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