# On the Frequency Factor in Electron Transfer Reactions and Its Role in the Highly Exothermic Regime

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## Abstract

Consideration of current information on the dependence of the electron transfer rate on the radial separation distance and on the reactants' radial distribution function suggests for adiabatic transfers a frequency factor closer to $10^{12}M^{-1}$ s$^{-1}$ than to $10^{11}M^{-1}$ s$^{-1}$. One effect is to raise the $\lambda$ values estimated from self-exchange rate constants, and to extend thereby the range of $\Delta G°$'s in which the "inverted region" is masked by a diffusion-controlled reaction rate.

## Introduction

The bimolecular rate constant of an electron transfer rate constant in solution is sometimes written as [1,2]

$$k_{act} = \kappa C e^{-\Delta G^*/kT} \tag{1}$$

where $C$ is a constant[1] which is frequently taken to be $\sim 10^{11}M^{-1}$ s$^{-1}$, the collision frequency at unit molar concentration in the gas phase. $\kappa$ is a factor which is unity for adiabatic electron transfers and less than unity for nonadiabatic ones. $\Delta G^*$ describes the free energy barrier to reaction. It contains work terms for bringing the reactants together and contains vibrational and solvent orientational terms, arising from a reorganization which permits the electron transfer to occur.

In the present paper we examine the value of $C$ more closely, taking into account some estimates of the radial distribution function and of the dependence of the electron transfer rate on the intervening separation distance $r$. We shall be more concerned with obtaining an order of magnitude estimate of $C$ rather than with attempting to evaluate precisely each of the factors that contribute to the bimolecular rate constant.

[1] The constant $C$ is the $\rho Z$ in [1, eq. (19)] and in [2, eq. (31)].

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## Theory

A detailed calculation of the electron transfer rate involves, among other things, a knowledge of the motion along the reaction coordinate, regardless of whether the reaction is electronically adiabatic or nonadiabatic [1]. Contributions to this motion can come from (i) intramolecular vibrations in the reactants, including any in their coordination shells, (ii) electrically polarized vibrations of the surrounding solvent molecules outside the coordination shells, (iii) orientational motions of those solvent molecules, and (iv) the translational motion of the approach of the two reactants [1].

When motion (iv) does not contribute significantly to the reaction coordinate,[2] one can calculate the bimolecular rate constant in two steps: one first calculates the reaction rate constant at fixed separation distance $r$, a first-order rate constant $k(r)$, and then suitably averages over all $r$. The averaging is particularly straightforward when the rate of diffusion is fast. Then the probability that the pair of reactants has a separation distance between $(r, r + dr)$ at any time equals essentially the equilibrium (no reaction) probability, $g(r)\, 4\pi r^2\, dr$. $g(r)$ is the equilibrium radial distribution function for the pair. One can then write the bimolecular reaction rate constant $k_{act}$ as

$$k_{act} = \int_0^\infty g(r) 4\pi r^2 k(r)\, dr \tag{2}$$

We have used the subscript "act" to denote "activation controlled rate constant." Later we return to the case where, instead, diffusion is a slow step.

It is convenient to write $k(r)$ in terms of an electronic transition probability factor $\kappa(r)$ (e.g., a velocity averaged Landau–Zener factor), a free energy barrier $\Delta G'(r)$,[3] and a mean frequency factor $\nu$ associated with motions (i)–(iii). $\Delta G'(r)$ depends on $r$ mainly via contributions (ii) and (iii) of the vibrational and orientational polarization of the solvent molecules [1,2]. Contribution (i) to $\Delta G'(r)$ is independent of $r$ [1,2] when the dependence of intramolecular vibrations of each reactant on $r$ is negligible. We now have

$$k(r) = \kappa(r) \nu e^{-\Delta G'(r)/kT} \tag{3}$$

We proceed to estimate $C$ from eqs. (2) and (3) by considering individually $g(r)$, $\kappa(r)$, $\nu$, and $\Delta G'(r)$. $g(r)$ is a damped oscillating function of $r$.

[2] That is, if $q$ denotes the reaction coordinate, $q$ then has contributions mainly from the coordinates in (i)–(iii). Only then is it meaningful, one can show, to speak of a first-order rate constant $k(r)$ for each fixed separation distance $r$. In hard sphere collision theory only (iv) contributes to the reaction coordinate.

[3] This term was denoted by $\Delta F^*(R)$ in [2, eq. (31)].

For purposes of making an estimate of the terms in eq. (2) we write $g(r)$ in a suggestive form:

$$g(r) = g_0(r)e^{-w(r)/kT} \tag{4}$$

where $g_0(r)$ is a largely geometric factor, being similar to the value it would have for an uncharged and nonspecifically interacting pair. All of the specific-interaction contributions to $g(r)$ are contained in what might be called the "work term" $w(r)$. $g_0(r)$ in a liquid rises sharply from a value of about zero in the short range repulsive potential region to a maximum, characteristic of the behavior of nearest neighbors, then falls to a value somewhat below unity, and then, after more oscillation, reaches a limiting value of unity at larger $r$ [3].

We write the sum of $w(r)$ and $\Delta G'(r)$ as $\Delta G^*(r)$:

$$\Delta G^*(r) = w(r) + \Delta G'(r) \tag{5}$$

The factor $\nu$ in eq. (3) is in units of $s^{-1}$ and is a mean of the frequencies of each of the motions (i)–(iii), each weighted by its contribution (one can show[4]) to $\Delta G'$. For example, if a coordinate does not contribute to $\Delta G'$, it does not contribute to $\nu$. Typical frequencies for (i), (ii), and (iii) are ~400 $cm^{-1}$ (for metal ligand bonds), ~200 $cm^{-1}$ (for the solvent water), and ~1 $cm^{-1}$ (again for water) [7]. The contributions of (ii) and (iii) to $\Delta G^*$ are estimated to be roughly equal [7], so that when weighted (iii) contributes negligibly to $\nu$ in the case of water as the solvent. The relative contribution of (i) and (ii) will vary from system to system, and we shall for concreteness select a mean $\nu$ of 300 $cm^{-1}$, which is about $10^{13}$ $s^{-1}$.

Several rather rough estimates have been made for the dependence of $\kappa$ on $r$, which in each case has an exponential dependence on $r$. We can then write

$$\kappa(r) = \kappa_0 e^{-\alpha(r-\sigma)} \tag{6}$$

where $\kappa_0$ is the value of $\kappa(r)$ at $r = \sigma$, and $\sigma$ is the value of $r$ where $g_0(r)$ has its maximum. If $\kappa_0$ is about unity, the reaction is usually termed adiabatic. When there are no intervening molecules between the two reactants, $\alpha$ has been estimated to be 2.6 $Å^{-1}$ [8]. When there are intervening molecules,

[4] See, for example, [4, chap. 3, eqs. (66) and (79)]. The reaction coordinate, if one uses a Fourier coordinate description of the solvent polarization [5] and a normal coordinate treatment of all other vibrations, is $\Sigma_i k_i Q_i a_i$ (when $k_i$ is taken to be the same for reactants and products), $a_i$ is equilibrium displacement of the $i$th coordinate due to reaction. $k_i a_i$ is seen to be the $\alpha_{ri}$ in eq. (66), more precisely the $\alpha_{1i}$ in eq. (79). We obtained the above form for the reaction coordinate by setting the potential energy of the reactants equal to that of the products plus a constant. The latter constant vanishes at the transition state. Different values of the latter constant generate a family of parallel hypersurfaces, on each of which the reaction coordinate has some constant value. This definition of a reaction coordinate is similar to that in the brief discussion involving the coordinates $\sigma$ and $\gamma$ following [6, eq. (A2)].

$\alpha$ has been estimated to be about 1.4 Å$^{-1}$ [9]. [Elsewhere, a more precise formula than (6) will be used, one which joins a nonadiabatic equation for $k(r)$ with an adiabatic equation at the $r$ where both are equal.]

In calculating the integral over $r$ in eq. (2), we consider these cases where there is not and where there is intervening material between the reactants.

The function $g_0(r)$ falls from its maximum (at $r = \sigma$) of between 2 and 3 to a value of about unity in a distance of about one half a molecular diameter or perhaps somewhat less.[5] If that diameter is about 6 Å, then $\exp(-\alpha r)$ is a more rapidly varying function of $r$ in the vicinity of $r = \sigma$ (it falls to $1/e$ of its value in 0.4 Å in the case of no intervening material). Taking $\Delta G^*(r)$ to be relatively slowly varying also, the integral in eq. (2) can be evaluated approximately by taking $g_0(r) = 0$ for $r < \sigma$, replacing $r^2$, $g(r)$, and $\Delta G^*(r)$ by their values at $r = \sigma$, and integrating from $r = \sigma$ to $\infty$. One obtains

$$k_{act} \cong g_0(\sigma) e^{-\Delta G^*(\sigma)/kT} 4\pi\sigma^2 \nu \kappa_0/\alpha \tag{7}$$

Using the previous estimate of $\nu \sim 10^{13}$ s$^{-1}$, $g_0(\sigma)$ of between 2 and 3, and $\alpha \sim 2.6$ Å$^{-1}$, one obtains for a pair of reactants, each of radius 3 Å,

$$k_{act} \sim 10^{12} \kappa_0 e^{-\Delta G^*(\sigma)/kT} M^{-1}\ \text{s}^{-1} \quad (\sigma = 6\ \text{Å}) \tag{8}$$

For larger reactants the numerical factor in eq. (8) is of course larger than $10^{12}$, since it is proportional to $\sigma^2$. For the case of an electronically adiabatic reaction $\kappa_0 \sim 1$.

When there is intervening material, the most probable $r$ is somewhat greater than $\sigma$, the mean $g_0(r)$ is less than $g_0(\sigma)$, $\alpha \sim 1.4$ Å$^{-1}$, and so the constant multiplying $\exp(-\Delta G^*/kT)$ in eq. (8) is still of the same order of magnitude. Thus a value of $10^{12} M^{-1}$ s$^{-1}$ appears to be a reasonable choice. For more specific assumptions more detailed estimates of $C$ in eq. (1) can be made.

It is useful in compare[6] this value of $10^{12} M^{-1}$ s$^{-1}$ for $C$ with the gas phase hard sphere collision frequency $Z = (8\pi kT/\mu)^{1/2}\sigma^2$, for molecules of reduced mass $\mu \sim 50$ and radius 3 Å. The latter equals $2 \times 10^{11} M^{-1}$ s$^{-1}$ at 300 K. Physically the reason why the value of $C$ is higher than $Z$ (some five times higher in the present estimate) is twofold. Collisions of hard spheres occur only on contact, while electron transfer can occur at various $r$ which are larger than the "contact distance" $\sigma$. Second the $g_0(\sigma)$ is larger than unity,[7]

[5] For example, [3b, Fig. 6]. Strictly speaking, we should use instead a $g_0(r)$ for a pair of solute molecules. When these solute molecules are much larger than the solvent's, $g_0(\sigma) \cong 1$.

[6] See footnote 1.

[7] See footnote 5.

the "dilute-gas" hard sphere value, although it can be close to unity if the solute molecules are appreciably larger than those of the solvent.

Thus far we have assumed diffusion to be rapid. If we use, in the first approximation, the estimate in eq. (7) for $k_{act}$, the observed rate constant is given in the steady state by eq. (9) for the case of no back reaction [10,11]:

$$\frac{1}{k_{obs}} = \frac{1}{k_{act}} + \frac{1}{k_{diff}} \tag{9}$$

where $k_{diff}$ is the diffusion-controlled rate constant. Its value depends on the charges of the reactants, being of the order of $10^{10} M^{-1}\ s^{-1}$ in water for uncharged species. When $k_{diff} \gg k_{act}$, $k_{obs}$ equals $k_{act}$, and equals $k_{diff}$ when $k_{act} \gg k_{diff}$.

In the so-called normal region, where the bimolecular rate constant increases with increasingly negative standard free energy of reaction $\Delta G°$ [2,6], the reorganizational term in $\Delta G^*(r)$ favors small $r$.[8] (The work term $w(r)$ in $\Delta G^*(r)$ favors small or large $r$, depending upon its sign.) The closer the reactants are together, the less the distant solvent molecules experience a change of potential energy, via a change in the local electric field, when the electron transfers, and so the less the need for solvent reorganization to occur, and so the smaller is $\Delta G^*(r)$.

In the so-called inverted region [6], which should occur at very negative $\Delta G°$, the bimolecular reaction rate constant decreases, instead, with increasingly negative $\Delta G°$ due to the difficulty in this region of intersection of the potential energy curves of the reactants with that of the products. A larger $r$ produces a larger solvent reorganizational term parameter $\lambda_0$ (in the notation of [12]), causes thereby an increased lateral displacement of the two surfaces, and permits them to intersect more easily in this highly exothermic region. Thereby in the "inverted" region an increased $r$ actually causes a decrease in $\Delta G^*$ [13]. The "inversion" will be less evident when this decrease in $\Delta G^*$ is large enough.

Some further words about the inversion region are in order. In a quantum mechanical treatment of the reorganizational motion, e.g., via the evaluation of Franck–Condon factors, only the intermolecular vibrations need to be treated quantum mechanically, since the frequency of the other coordinates is relatively low [7]. Moreover, using typical metal–ligand frequencies the quantum correction to the classically calculated reaction rate was found to be typically small in the normal region (from 20% to a factor of 4 in a recent calculation [7]). The nuclear tunneling was more noticeable in the inverted region [7], because that tunneling tended to decrease the tendency of the rate to decrease with increasing $-\Delta G°$ at very negative $\Delta G°$. This nuclear tunneling does not, however, cause the effect

[8] See the $1/R$ in the $\lambda_0$ of [12, eq. (A3)] or in [2, eq. (89)].

to disappear (see [13] and, e.g., [14]). In the field of radiationless transitions this effect of decreased rate with increased exothermicity is again very well known [15], and is termed there the "energy gap" law.

Some experimental evidence for the "inverted" effect has been offered [16,17]. Indeed, the preferential formation in other highly exothermic reactions of electronically excited states of products, instead of the more exothermically formed ground state products, would be a further manifestation of this effect.

The calculated inverted effect is less when one takes into account the higher estimate of the frequency factor ($10^{12}$ versus $10^{11} M^{-1}\,s^{-1}$) and the role discussed above of the dependence on $r$ of the solvent reorganizational contribution to the $\lambda$ in $\Delta G^*(r)$. The inverted effect is masked to some extent by the presence of $k_{diff}$ in eq. (9).

For many reactions which have been studied no evidence of the inversion has been obtained, e.g., [18–20]. In some cases alternate pathways may exist, hydrogen atom transfer, for example, or formation of electronically excited products. In others, where the rate has been inferred only from the quenching of fluorescence of one of the reactants, quenching may occur via an exciplex formation [21,22], rather than via electron transfer, when exciplex formation is possible. In others the calculated inverted effect may be less due to the two factors cited above. In still others, anharmonic effects can contribute to decreasing (or increasing) the rate, and high-frequency modes which play less of a role in the normal region may also contribute importantly to accepting the excess energy in the "inverted" region. The latter would reduce the tendency for $k_{obs}$ to decrease with increasingly negative $\Delta G°$ in the very negative $\Delta G°$ region.

There has been some tendency [23] to use an equation which was derived [24] originally for atom transfers.[9] This equation displays no inversion. However, except in the actual case of atom transfers, the application of such an equation must be regarded as purely empirical, at present, and to have no theoretical advantage over the frankly empirical Rehm–Weller equation [18].

As an example of the effect of using a value for $C$ in eq. (1) of $10^{12} M^{-1}\,s^{-1}$ instead of $10^{11} M^{-1}\,s^{-1}$, we consider the series of highly exothermic reactions [17]

$$(10) \qquad {}^*RuL_3^{2+} + ML'^{3+}_3 \rightarrow RuL_3^{3+} + ML'^{2+}_3$$

The asterisk denotes an electronically excited reactant, L and L′ are various permutations of the ligands bpy and mebpy, and M denotes Cr, Os, and Ru.

[9] An analogous equation is given in [25], and it has been pointed out [26, 27] that it is the same as that in [24].

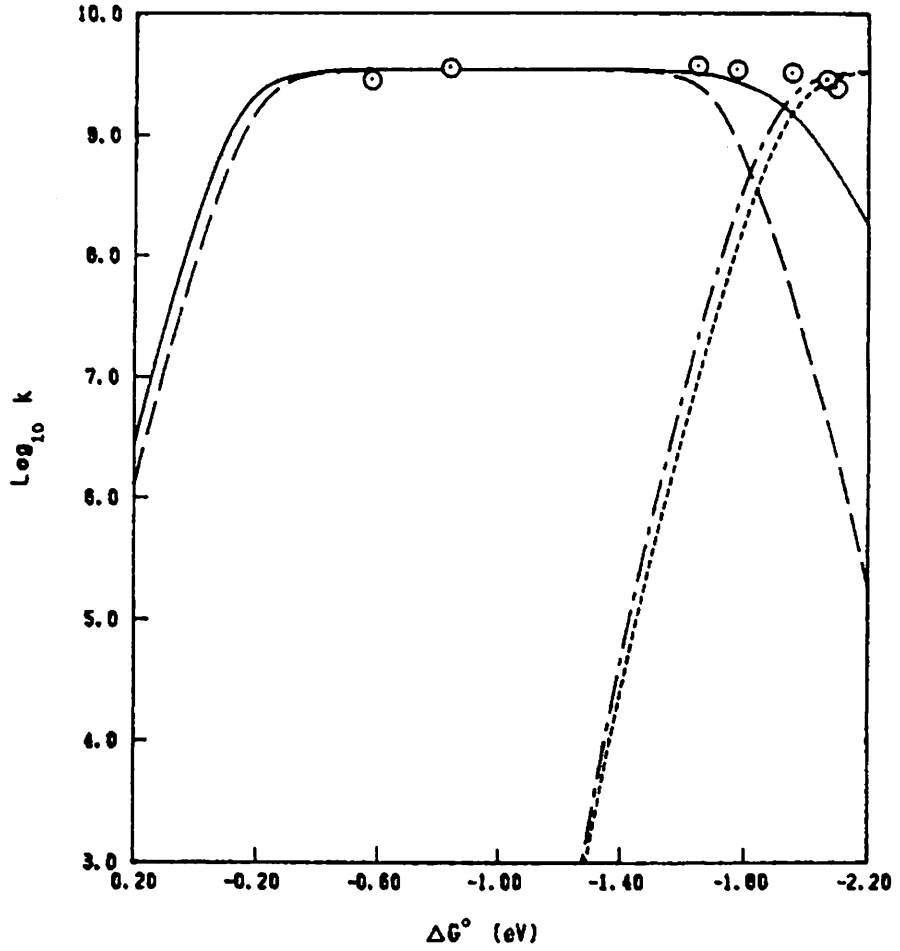


Figure 1. Experimental (open circles) and calculated rate constants for reaction (9) versus $\Delta G°$. Dashed line—classical result; solid line—quantum mechanical result; solid circles—quantum mechanical calculation to form an electronically excited product; dashed-dotted line—classical result to form an electronically excited product. Numerical constants used are given in [13], together with an identification of the individual reactants in the plot. The units of $k$ are $M^{-1}$ $s^{-1}$.

We use a $C$ of $10^{12}$ instead of the $10^{11}$ used in [13], and use a $\lambda_0$ which is greater than that used[10] in [13] by an amount $\Delta\lambda_0$,

$$e^{-\Delta\lambda_0/kT} = \frac{1}{10} \tag{11}$$

so as to give the same self-exchange rate constants. Figure 1 is obtained instead of [13, Fig. 3]. One sees, on comparison with [13, Fig. 3], that the results are now closer to the observed values in the highly exothermic region.

To study the effect of the dependence of $\Delta G^*(r)$ on $r$ in this inverted region, evaluation of the integral in eq. (2) will be made in a later paper.

The effects described herein may also be present in electrode reactions,

[10] Denoted by $\lambda_{out}$ in [13].

as will be discussed in a future paper. Very rapid reactions in solution or at electrodes (low $\Delta G^*$) frequently involve aromatic organic molecules [28]. The calculation of $\Delta G^*_{exp}$ from the rate constant [28], when $\Delta G^*_{exp}$ is small, is sensitive to the value of $C$.

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## Bibliography

[1] R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).
[2] R. A. Marcus, *J. Chem. Phys.*, **43**, 2654 (1965).
[3] (a) I. R. McDonald and M. L. Klein, *Faraday Discuss. Chem. Soc.*, **66**, 48 (1978); (b) P. A. Egelstaff, *Faraday Discuss. Chem. Soc.*, **66**, 7 (1978).
[4] N. B. Slater, "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, NY, 1959.
[5] V. G. Levich and R. R. Dogonadze, *Proc. Acad. Sci. USSR, Phys. Chem. Sec.* (Engl. transl.), **133**, 591 (1960).
[6] R. A. Marcus, *Discuss. Faraday Soc.*, **29**, 21 (1960).
[7] P. Siders and R. A. Marcus, *J. Am. Chem. Soc.*, **103**, 741 (1981).
[8] J. Jortner, *J. Chem. Phys.*, **64**, 4860 (1976).
[9] J. J. Hopfield, *Proc. Natl. Acad. Sci.*, **71**, 3640 (1974).
[10] R. A. Marcus, *Discuss. Faraday Soc.*, **29**, 129 (1960).
[11] R. M. Noyes, *Prog. React. Kinet.*, **1**, 129 (1961).
[12] R. A. Marcus, *Phys. Chem. Sci. Res. Rep.*, **1**, 477 (1975).
[13] P. Siders and R. A. Marcus, *J. Am. Chem. Soc.*, **103**, 748 (1981).
[14] J. Ulstrup and J. Jortner, *J. Chem. Phys.*, **63**, 4358 (1975).
[15] W. Siebrand, in "The Triplet State," A. B. Zahlan, Ed., Cambridge University Press, London, 1967, p. 31.
[16] A. J. Frank, M, Gratzel, A. Henglein, and E. Janata, *Ber. Bunsenges. Phys. Chem.*, **80**, 294, 547 (1980).
[17] C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **99**, 241 (1977).
[18] D. Rehm and A. Weller, *Ber. Bunsenges, Phys. Chem.*, **73**, 834 (1969).
[19] R. Ballardini, G. Varani, M. T. Indelli, F. Scandola, and V. Balzani, *J. Am. Chem. Soc.*, **100**, 7219 (1978).
[20] J. K. Nagle, W. J. Dressick, and T. J. Meyer, *J. Am. Chem. Soc.*, **101**, 3993 (1979).
[21] A. Weller and K. Zachariasse, *Chem. Phys. Lett.*, **10**, 590 (1971).
[22] J. Joussot-Dubien, A. C. Albrecht, H. Gerischer, R. S. Knox, R. A. Marcus, M. Schott, A. Weller, and F. Willig, *Life Sci. Res. Rep.*, **12**, 129 (1979).
[23] V. Balzani, F. Bolletta, and F. Scandola, *J. Am. Chem. Soc.*, **102**, 2152 (1980).
[24] R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).
[25] N. Agmon and R. D. Levine, *Chem. Phys. Lett.*, **52**, 197 (1977).
[26] J. L. Kurz, *Chem. Phys. Lett.*, **57**, 243 (1978).
[27] N. Agmon and R. D. Levine, *J. Chem. Phys.*, **71**, 3034 (1979).
[28] H. Kojima and A. J. Bard, *J. Am. Chem. Soc.*, **97**, 6317 (1975).

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