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Long-range Tunnelling Electron Transfer in Chemical Reactions

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We have generalised recent experimental and theoretical results on a process which is uncommon in classical chemistry: long-range tunnelling electron transfer. These reactions play an important role in various areas of chemistry and biochemistry, and they offer new pathways for controlling the direction of chemical change. 94 references.

CONTENTS

I. Introduction 518
II. Historical account of the discovery and study of long-range tunnelling electron transfer reactions 519
III. Models of the elementary act of long-range electron transfer 522
IV. Formal kinetics of tunnelling electron transfer reactions 523
V. Methods of calculating the kinetic characteristics of tunnelling reactions from experimental data 525
VI. Kinetic characteristics of long-range tunnelling electron transfer reactions 527
VII. Chemical reactions involving long-range electron transfer 528

I. INTRODUCTION

It has long been thought self-evident that bimolecular reactions can occur only when the interacting molecules are in direct contact, i.e. when the approach distance is equal to the sum of the gas-kinetic or crystallographic radii. However several reactions between particles separated by much larger distances (up to many tens of Ångstroms) have recently been discovered. The reacting species are separated either by molecules of the medium (condensed phase) or by a vacuum (gas phase).

These are the so-called tunnelling (or sub-barrier) long-range electron transfer reactions. During these reactions an electron passes (tunnels) through the energy barrier separating the reactants, which can be much higher than the intrinsic energy of the electron (several electron-volts). These transitions contravene the rules of classical mechanics, but they are permitted in quantum mechanics.

The quantum-mechanical tunnelling of particles through potential barriers was first postulated in physics to explain the ionisation of atoms in a strong electric field[1], the cold emission of electrons from metals[2], and the α-decomposition of atomic nuclei[3,4]. A simple formula was obtained[3] for the transition probability w per unit time of a particle of energy E below a potential barrier of height $U(x)$:

$$w = \nu_0 \exp\left(-\frac{2}{\hbar}\int_0^r |p|\,dx\right). \quad (1)$$

In this formula ν_0 is the collision frequency of the particle with the potential barrier, $p = \{2m[U(x) - E]\}^{1/2}$, m is the mass of the particle, and $\hbar$ is Planck's constant. Eqn. (1) can be written more simply

$$w = \nu_0 \exp(-2r/a), \quad (2)$$

where $a = \gamma\hbar/[2m(U_{max} - E)]^{1/2}$, U_{max} is the maximum value of $U(x)$ (the barrier height), $\gamma \simeq 1$ is a numerical coefficient depending on the shape of the barrier, and the distance r corresponds to the width of the barrier (see Fig. 1). It is evident from formula (2) that the probability of the tunnelling transition decreases exponentially as the mass of the particle increases. Hence the most effective tunnelling transitions can be expected in reactions involving the lightest of all chemical particles: the electron.

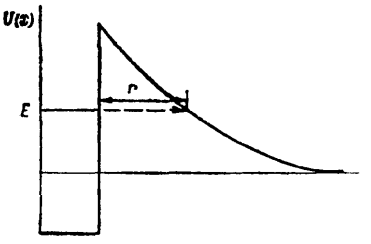


Figure 1. Tunnelling electron transfer through an energy barrier.

There have been many attempts to estimate the maximum distance through which an electron can tunnel in chemical reactions[5,6] (see also Ref. 7). All these calculations were based on formula (2), assuming a frequency ν_0 equal to the characteristic frequency of the motion of electrons in atoms ($\nu_0 \simeq 10^{15}$–10^{16} s^{-1}), and a barrier height U_{max} equal to the ionisation potential of the donor particle. These estimates are too approximate to confirm or deny with any reliability the hypothesis of long-range tunnelling transitions of electrons in chemical reactions. Their most serious shortcoming is that formula (2) was obtained for processes in which the particles can tunnel into a region of space possessing a continuous spectrum of energies: strictly speaking, this formula is not applicable to chemical reactions, in which the electron is transferred between states with discrete energy levels. Hence the concept of long-range electron transfer in chemical reactions did not gain wide acceptance until direct experimental evidence of the reality of this process became available.

The most convincing evidence of long-range electron tunnelling was obtained in studies of the low-temperature oxidation and reduction of solids. Typical of these processes are the reactions of trapped electrons (e^-_{tr}) with various acceptors (organic or inorganic molecules, ions, ion-radicals, and transition metal complexes). The rates of many of these reactions were found to be temperature-independent and much higher than the rate of diffusion-limited collisions between reactants.

Examples of long-range electron transfer reactions in the liquid phase include the reaction of hydrated electrons (e^-_{aq}) with various inorganic anions (CrO_4^{2-}, MnO_4^-, etc.) in dilute solutions. The effect of the electrostatic repulsion between like charges on the rate of these reactions is abnormally low, suggesting a large separation between the charges at the moment of reaction.

Typical gas-phase reactions involving a long-range electron transfer step are the reactions between alkali metal atoms and halogen molecules, for example

$$K + I_2 \rightarrow K^+ + I_2^- \rightarrow KI + I.$$

Measurements by the molecular beam method have shown that the interaction radii for these reactions can exceed the gas-kinetic radii by a factor of two.

II. HISTORICAL ACCOUNT OF THE DISCOVERY AND STUDY OF LONG-RANGE TUNNELLING ELECTRON TRANSFER REACTIONS

The reactions of alkali metal atoms with halogen molecules in the gas phase are the first reported example of chemical reactions at long range. Reaction cross-sections somewhat greater than the gas-kinetic cross-sections were observed in a study[8] of diffusion flames published in 1932. The correctness of this observation was confirmed by later, more precise measurements by the molecular beam method[9-11] carried out in the 1950's and 1960's. The following mechanism was proposed[12]: initially the reactants approach to within a distance such that the difference between the ionisation potential I_M of the metal atom and the electron affinity A_{X_2} of the halogen molecule is equal to the energy of the interacting unit charges, i.e.

$$I_M - A_{X_2} = e^2/r_c. \qquad (3)$$

At this instant the electron passes under the barrier from M to X_2. Immediately after the electron transfer the long-range Coulombic forces between M^+ and X_2^- begin to operate, making the particles approach each other until the ordinary chemical forces can break the X–X bond and form an M–X bond.

Table 1. Interaction radii r_e, distances r_c,[10] and sums of gas-kinetic radii of the reactants $r_M + r_{I_2}$ for the reactions between alkali metals and iodine (Na* is an excited sodium atom).

M	r_e, Å	r_c, Å	$r_M + r_{I_2}$, Å
K	6.3	5.26	4.2
Pb	7.3	5.63	4.4
Cs	7.6	6.43	4.6
Na	7.9	4.07	3.8
Na*	8.2	—	3.8

The interaction radii r_e calculated from the measured cross-sections for a series of reactions are compared in Table 1 with the distances r_c calculated by formula (3) and with the sums of the gas-kinetic radii of the reactants $r_M + r_{X_2}$. It can be seen that both r_e and r_c are greater than $r_M + r_{X_2}$, i.e. the electron transfer step occurs at distances beyond the range of chemical (exchange) forces.

The next important step was the discovery[13-16] of anomalously large rate constants for the diffusion-controlled reactions of hydrated electrons with various inorganic anions in aqueous solutions. Table 2 lists the highest observed rate constants (k_e) for reactions between e^-_{aq} and inorganic anions and cations, and also the theoretical diffusion-limited rate constants (k_D) for the same reactions, calculated by the Debye formula[17] from the known radii and diffusion coefficients of the reactants[16]

$$k_D = 0{,}004\pi N D\sigma\,(z_A e^2/\varepsilon kT\sigma)\,[\exp(z_A e^2/\varepsilon kT\sigma) - 1]^{-1}. \qquad (4)$$

Table 2. Maximum reported values of the rate constants k_e and of the diffusion constants k_D for the reactions of e^-_{aq} with anions and cations[16] (en is ethylenediamine, EDTA is the ethylenediaminetetra-acetate ion).

Acceptor	$10^{10}k_e$, litre mole^{-1} s^{-1}	$10^{10}k_D$, litre mole^{-1} s^{-1}
$Co(NO_2)_6^{3-}$	3.2—5.8*	0.27
$Co(C_2O_4)_3^{3-}$	1.3	0.27
$Co(CN)_5Cl^{3-}$	1.8*	0.19
$Cr(C_2O_4)_3^{3-}$	1.8*	0.25
$Cr(EDTA)^-$	2.6*	1.2
$Cr_2O_7^{2-}$	3.3	0.53
CrO_4^{2-}	1.8	0.33
$Mn(CN)_6^{4-}$	0.54	0.068
$Fe(CN)_5NO^{2-}$	2.4	0.50
MnO_4^-	2.2	0.94
O^-	2.2	0.86
NO_3^-	0.85	0.52
$Co(NH_3)_6^{3+}$	8.2	9.2
$CO(NH_3)_5Br^{2+}$	6.2	6.2
$Co(en)_2CO_3^+$	4.9	4.4
$Cr(H_2O)_6^{3+}$	6.2	6.9
$Cr(NH_3)_5Cl^{2+}$	6.2	6.4
$Cr(en)_3^{3+}$	7.8	9.2
$Cr(en)_2(NCS)_2^+$	4.2	4.4
$Os(NH_3)_6^{3+}$	7.2	8.9
$Rh(NH_3)_6^{3+}$	7.9	8.9

*Experimental value; the k_e values for all the other acceptors in the Table are extrapolated to zero ionic strength in the solution.

In this formula $z_A e$ is the charge on the acceptor, $D = D_A + D_e$ refers to the diffusion coefficients of the acceptor and of e^-_{aq}, σ is the distance between the reactants at the instant of electron transfer, $\epsilon = 81$ is the dielectric constant of water, N is Avogadro's number, k is Boltzmann's constant, and T is the temperature. In the calculation of k_D it was assumed that electron transfer occurs by direct collision between the reactants i.e. that $\sigma = r_A + r_e$ where r_A and r_e are the radii of the reactants. It is clear from Table 2 that the largest values of k_e for the reactions of e^-_{aq} with anions are similar to the k_e values for the reactions of e^-_{aq} with cations, and much greater than the k_D constants calculated by formula (4). The relative insensitivity to electrostatic repulsion effects of the rate of the reaction of e^-_{aq} with anions was taken as evidence that fast reactions of this type take place at distances in excess of the sum of the radii of the reactants.

Nevertheless the experimental evidence for long-range electron transfer in liquids and gases was too limited for a wide recognition of the importance of long-range interactions in chemistry. In view of the complexity of the molecular beam method, the observed difference between the interaction radii and the sum of the gas-kinetic radii ($r_M + r_{X_2}$) did not seem unduly large for the gas-phase reactions examined. In the reactions of e^-_{aq} with anions a weak electrostatic repulsion effect on the rate of the association of charged particles with their counter-ions could not be totally excluded.

Decisive proof of the existence of long-range tunnelling electron transfer processes was obtained only recently, from studies of oxidation–reduction reactions in solid matrices at low temperatures, i.e. under conditions where the diffusion of reactants and their mutual approach to within short distances can be rigorously excluded. Under these conditions long-range tunnelling electron transfer becomes the only possible mechanism for the reaction, and it can be observed and investigated unambiguously.

In 1965 it was found[18] that the trapped electrons (e^-_{tr}) formed by the γ-radiolysis of 2-methyltetrahydrofuran (2-MTHF) disappear slowly at 77 K. The decay of the e^-_{tr} species was ascribed[19] to a tunnelling reaction with hole centres, and a tunnel mechanism was proposed[20] for the disappearance of e^-_{tr} in an aqueous alkali glass containing additives. The Gamow formula (2) has been used[19,21] to calculate the distances to which electrons can tunnel in low-temperature radiation-chemical reactions (several tens of Ångstroms).

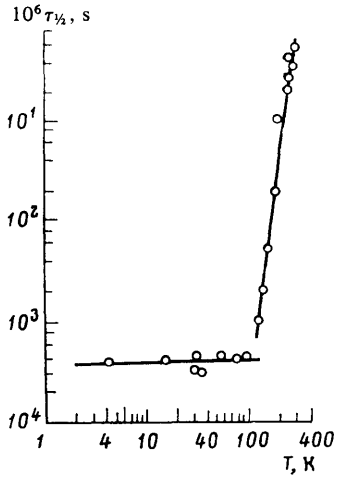


Figure 2. Characteristic time $\tau_{1/2}$ against temperature for the transfer of an electron from the reduced form of cytochrome *c* to the oxidised form of chlorophyll in *Chromatium D* bacteria.

However none of these results[18-20] definitely excluded the possibility of a diffusional mechanism for the disappearance of e^-_{tr}, or of a reaction with acceptors in direct contact with the trapped charge. Furthermore the use of Gamow's formula raises some objections (as was pointed out above). Nevertheless the work[19-21] stimulated further research in this area.

The first definitive formulation of the importance of tunnelling processes appeared in a paper by Chance and DeVault[22], who studied the temperature dependence of the characteristic time $\tau_{1/2}$ for the transfer of electrons from the reduced form of cytochrome *c* to the oxidised form of chlorophyll in *Chromatium D* bacteria over a wide range of temperature (300–4.2 K). They found a normal Arrhenius dependence at the higher temperatures ($T > 130$ K), but at $T < 130$ K $\tau_{1/2}$ was independent of temperature (see Fig. 2). Hence a diffusion-limited mechanism could be rigorously excluded, at least at $T < 130$ K. A detailed theoretical analysis of the electron transfer process in this system is given in a later paper[23]. However, as before, direct contact between the active centres of cytochrome *c* and those of chlorophyll in the bacteria at the instant of reaction could not be entirely excluded.

A tunnel mechanism for the electron transfer process was proposed also to explain[24-26] the temperature-independent luminescence produced by electron–hole recombination in γ-irradiated alkali halide crystals. The model[27,28] proposed to explain similar effects assumes that the recombination of donor–acceptor pairs in semiconductors also takes place by a tunnel mechanism. However the distance to which the electron is transferred in real systems was, again, unknown.

The first direct experimental demonstration[29] of a reaction between donors and acceptors a large distance apart was the reaction between e^-_{tr} and the anion-radical O^-. Both particles are formed, in equal yield, by the low-temperature radiolysis of frozen aqueous alkaline solutions, and they can be monitored through their characteristic optical (e^-_{tr}) and ESR (e^-_{tr} and O^-) spectra. It was possible to show from the width of the ESR spectral line that the distance between the reacting particles could not be less than 20 Å for most of the reacting pairs[30]. Also, the e^-_{tr} and O^- species were found to decay at the same rate even at very low temperatures. The kinetic curves for different temperatures are indistinguishable within experimental error over a wide range of time (five orders of magnitude), and they are linearised in an unusual set of coordinates (concentration against logarithm of time, see Fig. 3). A diffusion-limited mechanism for this process is excluded by the coincidence of the kinetic curves for different temperatures, and the distance between the reactants confirms the reality of the long-range electron transfer process. The unusual type of kinetic equation was simply explained by the distribution of distances $e^-_{tr}...O^-$ between the reacting pairs (see below).

Temperature-independent kinetics (at $T = 77.66$ and 4.2 K) were reported shortly afterwards[31] for the luminescence quenching process involving the recombination of e^-_{tr} with a biphenyl cation in a methylcyclohexane glass.

A detailed analysis[32] of the effect of added acceptors on the yield of ionic radiolysis products (e^-_{tr} and anion-radicals) revealed satisfactory agreement with the tunnelling electron transfer mechanism for the formation and disappearance of these particles. In particular it was found that the disappearance of e^-_{tr} in 2-MTHF doped with naphthalene (Nh) is accompanied by the formation of the Nh^- anion-radical in corresponding amounts (by the reaction $e^-_{tr} + Nh \rightarrow Nh^-$). The kinetic curves for this reaction at 77 and 87 K were indistinguishable.

Because of the logarithmic time-dependence of the concentration of reactants quantitative kinetic studies of tunnelling electron transfer reactions in solid matrices must extend over very long periods. For example, the reaction between e^-_{tr} and O^- had to be monitored over 5

orders of magnitude of time (see Fig. 3). Hence the development of pulsed techniques for measuring the kinetics of low-temperature reactions between active intermediates in radiolysis over many orders of magnitude, including very short times (from 10^{-6} to 10^{2} s), has played a very important role in subsequent studies of tunnelling electron transfer reactions[32]. Pulsed apparatus has been used to measure the kinetics of the reaction of e^-_{tr} with many different acceptors[32,33]. By combining measurements made in this apparatus with more traditional measurements over long periods the kinetics of the reaction

$$e^-_{tr} + Cu\,(en)_2^{2+} \rightarrow Cu\,(en)_2^{+} \qquad (5)$$

(where en is ethylenediamine) have been studied quantitatively over time intervals between 10^{-6} and 10^{6} s.[34,58]

The next important stage in the study of long-range electron transfer reactions was the development of special kinetic equations[35-47], including equations for paired[35,39,46], random[37-39], and arbitrary[35,38,46] distributions of reactants in the absence of diffusion, and also in the presence of diffusion for a random[40-42,44] or an arbitrary[43,45,47] distribution of reactants. It was shown that these equations give an accurate description of the observed kinetics of tunnelling reactions over the whole range of reaction times[58]. As an example we show in Fig. 4 the experimental (points) and the theoretical (lines) kinetic curves for the reaction between e^-_{tr} and $Cu(en)_2^{2+}$ at different concentration of $Cu(en)_2^{2+}$. This agreement between theory and experiment provides an important confirmation of the tunnel mechanism of the reaction.

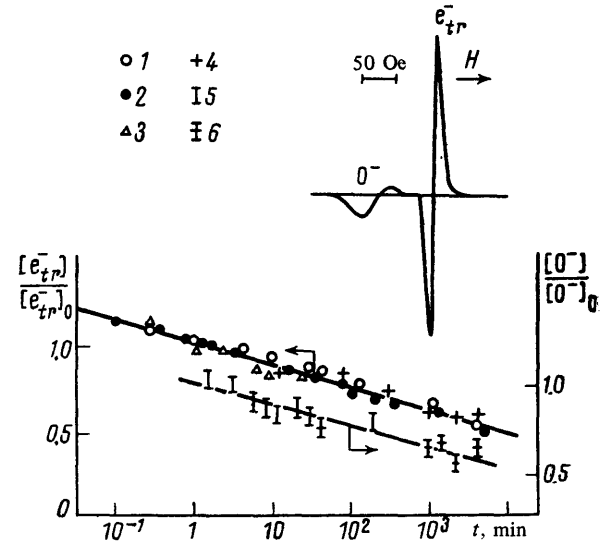


Figure 3. ESR spectra and decay curves for e^-_{tr} and O^- in 10 *M* aqueous NaOH; $[e^-_{tr}]_0$ and $[O^-]_0$ are the concentrations at $t_0 = 1$ min; *1*),*2*),*3*), and *5*) β-radiolysis, *4*) and *6*) γ-radiolysis; *D* values *1*) 3×10^{19}, *2*) 3.6×10^{20}, *3*)–*6*) 1.2×10^{20} eV cm^{-3}; *1*),*2*),*5*),*6*) 77 K, *3*) 120 K, *4*) samples stored at 4.2 K but irradiated and measured at 77 K.

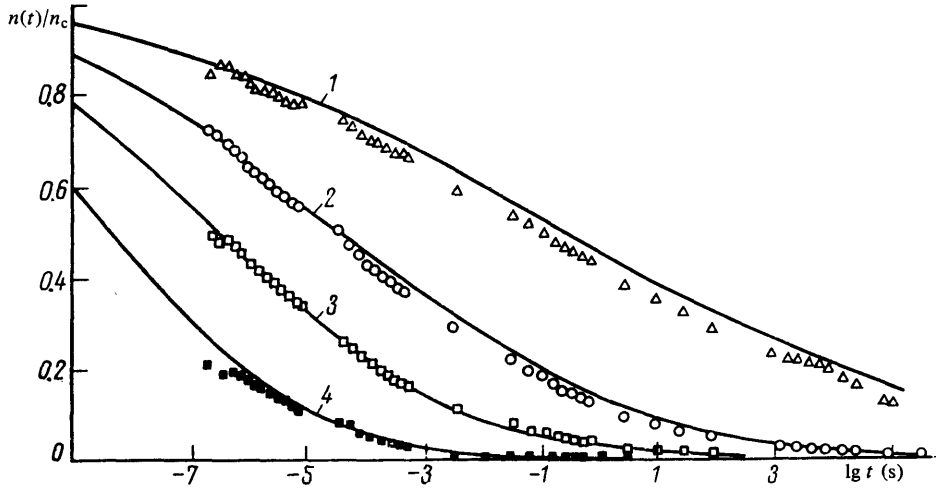


Figure 4. Kinetic curves for the reaction between e^-_{tr} and $Cu(en)_2^{2+}$ in 10 *M* aqueous NaOH solution at 77 K for different concentrations of $Cu(en)_2^{2+}$: *1*) 0.005, *2*) 0.01, *3*) 0.05, *4*) 0.1 *M*. The points are experimental, the curves are theoretical calculations by Eqn. (26) with the values $\nu = 10^{15.2}$ s^{-1} and $a = 1.83$ Å.

As long as long-range electron transfer had been observed only in the low-temperature reactions of e^-_{tr} there remained a doubt that the mechanism could be specific for this particle only, and that an alternative explanation could be delocalisation of e^-_{tr} (as in the case of polarons) over a large number of centres in solid matrices. Therefore the discovery of charge transfer over large distances in the low-temperature reactions of ordinary chemical species (inorganic anion-radicals and transition metal compounds) was the next important step[48,49]:

$$O^- + Fe(CN)_6^{4-} \rightarrow O^{2-} + Fe(CN)_6^{3-}, \quad (6)$$

$$SO_4^- + FeSO_4 \rightarrow SO_4^{2-} + FeSO_4^+, \quad (7a)$$

$$SO_4^- + AgNO_3 \rightarrow SO_4^{2-} + AgNO_3^+. \quad (7b)$$

The list of reactions of this type grew rapidly, and it now includes electron transfer processes from inorganic anion-radicals to organic molecules[50,51], from electronically excited molecules to various acceptors[52-54], between compounds of metals of variable valency[49,55], and from F-centres to hole centres in crystals[56] (see also Refs. 24-26).

The logical extension of this work was a quantitative analysis of the accumulated kinetic data[57,58] and a detailed theoretical discussion of the mechanism of the elementary act of the long-range tunnelling electron transfer process in solids[23,58-60].

Thus significant progress has been made in the study of long-range tunnelling electron transfer reactions. In this review we shall examine the theory of these processes, and we shall analyse existing kinetic data uniquely from the standpoint of this theory.

III. MODELS OF THE ELEMENTARY ACT OF LONG-RANGE ELECTRON TRANSFER

The simplest model used to describe long-range electron transfer reactions involves the tunnelling of an electron from a potential well through an energy barrier $U(x)$ (see Fig. 1). This model leads to formulae (1) and (2) for the variation of the transition probability per unit time with distance. According to this model the frequency ν_0 in Eqn. (2) is the characteristic frequency of the motion of electrons in atoms, i.e. $\nu_0 \simeq 10^{16}$ s^{-1}. The model also assumes that the parameters ν_0 and a are fully determined by the initial state of the system, i.e. the properties of the electron donor and those of the medium, and are independent of the final state, i.e. the properties of the electron acceptor. However both these predictions of the model were found to be incompatible with experimental results, since both ν_0 and a in practice depend on the nature of both the donor and the acceptor. For example, ν_0 can vary from 10^6 to 10^{21} s^{-1} for different reactions[58] (see Tables 3 and 4. But in spite of these shortcomings of the model formula (2) in general gives a correct qualitative description of the variation of w with r.

More exact models of tunnelling electron transfer between particles A^- and B in a solid,

$$A^- + B \rightarrow A + B^- \quad (8)$$

have been proposed[23,58-60]. The qualitative difference between these models and the previous model is the inclusion of the interaction (important in principle) between electronic and nuclear degrees of freedom in the molecules of the reactants and of the medium. As a result of this interaction the transition probability is substantially influenced by the motion of the nuclei of the reacting molecules and of the intervening molecules of the medium. Energy conservation is preserved by the transformation of the energy set free by the electron transfer into vibrational energy of the nuclei.

The newer models[23,58-60] differ in the type of nuclear motion assumed. Some workers[23,59,60] use the harmonic approximation to the vibration of the nuclei, whereas we have allowed for strong anharmonicity of the nuclear motion[58]. The model proposed in Ref. 58 gives a fuller physical description of long-range tunnelling electron transfer, and is fully consistent with all available experimental data. The transition probability of an electron per unit time is expressed as

$$w = \sum_i \sum_f p_i w_{if}. \quad (9)$$

The summation is taken over all the initial (i) and the final (f) states of the nuclear motion. In this expression p_i is the probability of an initial state i of energy E_i:

$$p_i = e^{-E_i/kT} / \sum_i e^{-E_i/kT}, \quad (10)$$

and w_{if} is the probability of a transition from the initial state i to the final state f. The variation of w_{if} with distance is given, as before, by the simple exponential function

$$w_{if} = \nu_{if} \exp(-2r/a_{if}). \quad (11)$$

This dependence arises, as in the case of the simplest model of tunnelling, from the exponential damping of the electronic wave functions in a classically inaccessible region of space. The ν_{if} values for different i or f in formula (11) should be different, in general. The a_{if} values are identical for all states of nuclear motion corresponding to the same electronic energy level, and they can vary only as a result of a change in electronic state. Hence in transfer processes not involving excited states Eqn. (9) simplifies to a form identical to Eqn. (2), i.e.

$$w = \nu \exp(-2r/a), \quad (12)$$

where $\nu = \sum_i \sum_f p_i \nu_{if}$.

However the parameters a_{if} and ν_{if} have a physical significance entirely different from that of the parameters a and ν_0 used in the simplest model. The parameter a is the half-sum of the Bohr radii of the electron in the initial (a_{A^-}) and the final (a_{B^-}) state in a medium of dielectric constant ϵ:

$$a = \frac{1}{2}(a_{A^-} + a_{B^-}), \quad (13)$$

which can also be written

$$a = \frac{1}{2}\varepsilon^{1/2}(a^0_{A^-} + a^0_{B^-}), \quad (14)$$

where $a^0_{A^-}$ and $a^0_{B^-}$ are the Bohr radii of the centres A^- and B^- in a vacuum. The subscripts i and f have been omitted in Eqns. (13) and (14). It can be seen from Eqn. (14) that the parameter a is symmetrically dependent on the properties of both the initial and the final state of the system, and also on the properties of the medium.

The parameter ν is a complex combination of the characteristics of electronic and nuclear motions in the system, and cannot be interpreted simply as the collision frequency of the electron with the potential barrier. According to our calculations ν can be vanishingly small under unfavourable conditions, and under favourable conditions it can exceed the characteristic frequency of the motion of electrons in atoms and be as high as 10^{22} s^{-1}.[58]

We note from Eqn. (9) that at low temperatures (when only the lowest initial state i is populated) the rate of an exothermic electron transfer reaction is independent of temperature:

$$w = \sum_f w_{0f}. \tag{15}$$

However at higher temperatures w can depend on T: depending on the relative probabilities of electron transfer from the ground state and from an excited state, w can either increase or decrease with increase of T.[58,61] The quantity

$$\tau = [w(r)]^{-1} = \nu^{-1}\exp(2r/a) \tag{16}$$

is the characteristic time for the tunnelling of the electron to a distance r. Eqn. (16) leads to the following expression for the average distance R_t to which the electron can tunnel in time τ:

$$R_t = (a/2)\ln \nu\tau. \tag{17}$$

Because of the exponential dependence of w on r the transition probability of the electron in time τ is almost unity for $r < R_t$ and close to zero for $r > R_t$.

IV. FORMAL KINETICS OF TUNNELLING ELECTRON TRANSFER REACTIONS

According to formula (12) the probability of a tunnelling transition for the electron decreases rapidly as the distance r between the reacting particles increases. In a typical situation (condensed medium) there is a distribution of the distance r between the reactants, leading to an unusual type of overall reaction kinetics: the variation of concentration $n(t)$ with time t is described by complex functions having $\lg t$ as their argument (see below). The specific form of these functions depends on the spatial distribution of the reactants and on the relative rates of tunnelling transitions and of diffusion.

A fruitful approach in the development of kinetic equations for tunnelling reactions was the use of equations for the normal concentrations of donors $n(r,t)$ and acceptors $N(r,t)$: the concentrations of donors $n_i(r,t)$ and acceptors $N_i(r,t)$ at a distance r from an arbitrarily chosen (i-th) acceptor (or donor) particle averaged at time t over the ensemble of particles of the opposite kind[62,63]:

$$n(r,t) = \sum_{i=1}^{N(t)} n_i(r,t), \tag{18}$$

$$N(r,t) = \sum_{i=1}^{n(t)} N_i(r,t). \tag{19}$$

In these expressions $n(t)$ and $N(t)$ are the volume average concentrations of donors and acceptors. The nominal and the volume average concentrations are related by the expressions[62]

$$n(t) = \lim_{r\to\infty} n(r,t), \tag{20a}$$

$$N(t) = \lim_{r\to\infty} N(r,t), \tag{20b}$$

$$n(t)\cdot N(r,t) = N(t)\cdot n(r,t), \tag{21}$$

$$n(0) - n(t) = N(0) - N(t), \tag{22}$$

where $n(0)$ and $N(0)$ are the average concentrations of donors and acceptors at zero time.

By assuming that each donor can react with an arbitrary acceptor, and that diffusional approach between the reactants can take place in parallel with the direct tunnelling transition, we arrive at the following equation for the nominal and the average concentrations as a function of time[45]

$$\frac{\partial}{\partial t}n(r,t) = -\left[w(r) + \int_0^\infty w(\rho)\,4\pi\rho^2 N(\rho,t)\,d\rho\right]n(r,t) + \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial n(r,t)}{\partial r}\right), \tag{23a}$$

$$\frac{\partial}{\partial t}N(r,t) = -\left[w(r) + \int_0^\infty w(\rho)\,4\pi\rho^2 n(\rho,t)\,d\rho\right]N(r,t) + \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial N(r,t)}{\partial r}\right), \tag{23b}$$

$$\frac{d}{dt}n(t) = -\int_0^\infty w(\rho)\,4\pi\rho^2 N(\rho,t)\,d\rho\, n(t), \tag{24a}$$

$$\frac{d}{dt}N(t) = -\int_0^\infty w(\rho)\,4\pi\rho^2 n(\rho,t)\,d\rho\, N(t). \tag{24b}$$

The general analytic solution of the system (23)–(24) is very cumbersome[45], but a much simpler solution is obtained by ignoring the diffusional mechanism:

$$\frac{n(t)}{n(0)} = \frac{1 - N(0)/n(0)}{1-[N(0)/n(0)]\exp\left\{[1-n(0)/N(0)]\int_0^t\int_0^\infty w(\rho)\exp[-w(\rho)t]\,N(\rho,0)\,4\pi\rho^2\,d\rho\,dt\right\}}. \tag{25}$$

For the most important case (in practice) of a random distribution of reactants, when $N(r,0) = N(0)$, we obtain from (12) and (25)

$$n(t)/n(0) = \exp[-(\pi a^3/6)N(0)\ln^3 \nu t] \tag{26}$$

in the case of $N(0) \gg n(0)$, and

$$n(t)/n(0) = [1 + n(0)(\pi a^3/6)\ln^3 \nu t]^{-1} \tag{27}$$

in the case of $N(0) = n(0)$.

The physical significance of Eqns. (26) and (27) is clear. The quantity $R_t = (a/2)\ln \nu t$ is the average distance to which the electron can tunnel in time t (see above). Hence the quantity $\exp[-(\pi a^3/6)N(0)\ln^3 \nu t] \equiv \exp[-(4\pi/3)N(0)R_t^3]$ in the right-hand side of Eqn. (26) is the probability of finding a donor particle outside the effective reaction volume $V_t = (4/3)\pi R_t^3$ surrounding an arbitrary acceptor particle, i.e. the probability that the particle will not disappear as a result of a tunnelling reaction at time t.

Eqn. (27) can be rewritten

$$1/n(t) - 1/n(0) = (4/3)\pi R_t^3. \tag{28}$$

This equation expresses the fact that the increase in time t of the mean volume associated with a single donor particle, $\Delta V = [n(t)]^{-1} - [n(0)]^{-1}$, is $(4/3)\pi R_t^3$.

Most experiments on the kinetics of tunnelling reactions have been made in glassy solutions, in which the spatial distribution of reactants was approximately random and the concentration of one of the reactants was usually much greater than that of the other. The results agree well with Eqn. (26), as shown by the experimental and the calculated kinetic curves for reaction (5) which are compared in Fig. 4. The calculated curves were obtained by Eqn. (26), the parameters a and ν being chosen so as to optimise the agreement between calculation and experiment. It is clear from Fig. 4 that the kinetics of reaction (5) can be described quantitatively over a wider range of time (12 orders of magnitude) and at concentrations $N(0) = 0.1$–0.01 M $Cu(en)_2^{2+}$ by selecting only two parameters. This means

that Eqn. (26) correctly describes the quantitative dependence of the concentration $n(t)$ both on time t and on the concentration of the other reactant $N(0)$. The optimum values of the parameters (a_{opt} = 1.83 Å and $\nu_{opt} = 10^{15.2}$ s^{-1}) are entirely reasonable in the light of other theoretical considerations.

Another practically important case is that of a paired distribution of reactants. Kinetic equations for tunnelling reactions between isolated donor–acceptor pairs cannot be obtained from Eqns. (23) and (24) because the concept of a nominal concentration is meaningless for isolated pairs. Kinetic equations for the tunnelling recombination of isolated pairs were obtained[29] by assuming a rectangular distribution of the pairs with respect to distance r, and also by assuming an arbitrary distribution[35].

If the distribution of the pairs in distance is described by the function $f(r)$ the change with time of the number $dn(t)$ of pairs separated by a distance between r and $r + dr$ is given by

$$\frac{\delta}{\delta t}[dn(t)] = -w(r) \cdot dn(t). \qquad (29)$$

Integrating Eqn. (29) with respect to time and using the initial condition $dn(0) = n(0) \cdot f(r) \cdot dr$ (where $n(0)$ is the total number of pairs at $t = 0$) we obtain

$$dn(t) = n(0) \exp[-w(r)t] \cdot f(r) \cdot dr. \qquad (30)$$

Integration of Eqn. (30) with respect to r gives an expression for the time-change of the number of donor–acceptor pairs $n(t)$:

$$n(t)/n(0) = \int_0^\infty \exp[-w(r)t] \cdot f(r) \cdot dr. \qquad (31)$$

For a rectangular distribution of the pair separations we have

$$f(r) = \begin{cases} (r_{max} - r_{min})^{-1} & \text{for } r_{min} \leqslant r \leqslant r_{max}, \\ 0 & \text{for } r > r_{max};\ r < r_{min}. \end{cases} \qquad (32)$$

Under the conditions $\ln \nu t \gg 1$ and $r_{max} \gg R_t \gg r_{min}$ we obtain from Eqns. (32) and (31)

$$n(t)/n(0) = [r_{max} - (a/2)\ln(\nu t)]/(r_{max} - r_{min}). \qquad (33)$$

Like Eqns. (26) and (27), Eqn. (33) has a clear physical meaning. It expresses the fact that for a rectangular distribution in r the fraction of the particles which do not undergo recombination at time t is $(r_{max} - R_t)/(r_{max} - r_{min})$.

As shown in Fig. 3, Eqn. (33) accurately describes the kinetics of the recombination of the e^-_{tr} and O^- particles formed in equal yield during the radiolysis of aqueous alkaline glasses.

1. Effect of an Electric Field on the Kinetics of Tunnelling Recombination

Formula (12) applies for an isotropic configuration of the function $w(r)$. However $w(r)$ can become anisotropic in the presence of an electric field: the energy barrier opposing electron transfer is raised in the direction of the field and lowered in the opposite direction. Under these conditions the parameter a in Eqn. (12) is smaller for transfer in the direction of the field than in the opposite direction. In principle the parameter ν also can be altered by the shift in the energy levels of the initial and the final state produced by the application of the field. However, in practice, we only need to be concerned with the effect of the field on the parameter a. The following formula for the transition probability in a constant electric field E has been proposed[46] to replace Eqn. (12) when the parameter a is asymmetric:

$$w(r) = \nu \exp[(2r/a_0) - (r^2 e E \cos\theta)/(2a_0 V_0)], \qquad (34)$$

where a_0 is the value of a in the absence of the field, e is the electronic charge, θ is the angle between the direction of electron transfer and that of the field, and V_0 is a parameter which characterises the binding energy of the electron to the centres A and B. In the derivation of Eqn. (34) it is assumed that the change in the interaction energy of the electron with the electric field produced by the transfer from the donor to the acceptor is small in comparison with V_0.

By inserting Eqn. (34) into (25) or (31) we obtain kinetic equations for tunnelling reactions in the presence of a field. In this way expressions were obtained[46] for the change with time of the luminescence intensity produced by the tunnelling recombination of donors and acceptors in paired

$$I(t) = A\{f[(a_0/2)\ln(\nu t)]/4\ln b\} \cdot (1/x\tau) \cdot \ln[(1 + bx)/(1 + x/b)] \qquad (35)$$

or in unpaired arbitrary distributions

$$I(t) = AN[(a_0/2) \cdot \ln(\nu t), 0] \cdot (\pi a_0^3/2x\tau) \cdot [\ln^2(\nu\tau)/2\ln b] \times \times \ln[(1 + bx)/(1 + x/b)] \cdot [n(t)/n(0)] \cdot [N(t)/N(0)]\,. \qquad (36)$$

In these expressions (which apply for $t > \tau$) the parameter τ is the time between the beginning of the tunnelling reaction and the application of the electric field, $f(r)$ is the initial distribution function of the distance between particles in a pair, $N(r, 0)$ is the initial arbitrary concentration of acceptors, $x = (t - \tau)/\tau$, and

$$b = \exp[(a_0 E e/8V_0)\ln^2(\nu t)].$$

It can be seen from Eqns. (35) and (36) that the kinetics of luminescence quenching by the application of a field are entirely determined by the spatial distribution of the reactants and by the parameter b, which can be evaluated from the discontinuous change in luminescence intensity at the instant when the field is applied[46].

Eqn. (35) has been used[46] to analyse results[64] on the influence of a field on the quenching kinetics of the luminescence due to the paired tunnelling recombination of e^-_{tr} with its counter-ion (the cation of tetramethyl-*p*-phenylenediamine) in glassy 3-methylpentane. The distribution function of the electron to counter-ion distances found in this way.

2. Kinetic Equations for Tunnelling Reactions in the Presence of Diffusion of Reactants

Diffusion can influence the kinetics of these reactions because it affects the spatial distribution of the reactants.

A general solution of the system of equations (23)–(24) has been obtained[45]. In the practically important case of a random distribution of reactants and $N(0) \gg n(0)$ the solution has a simple form for the two limiting cases of $t \gg \tau_D$ and $t \ll \tau_D$ (where $\tau_D = a^2/D$ is the time for the diffusion of the reactants to a distance of the order of a). For $t \ll \tau_D$ (slow diffusion) the kinetics of the tunnelling reactions are described by Eqn. (26), and for $t \gg \tau_D$ (fast diffusion) by the equation

$$n(t)/n(0) = \exp\left[-\frac{4}{3}\pi R^3 N(0) - 4\pi R D N(0)\, t\right], \qquad (37)$$

where $R = \frac{1}{2}a\ln(\nu\tau_D)$ is the tunnelling distance in time τ_D.

As can be seen from Eqn. (37) the disappearance of the donors in this situation is described by the ordinary kinetic law for first-order reactions (the second term in the exponential). The two terms in the exponential of Eqn. (37) correspond to two possible mechanisms for the disappearance of reactants at time t. Thus, for a donor and an acceptor particle at a distance $r < R$ we have $[w(r)]^{-1} < \tau_D$, and electron transfer is the faster process, whereas for $r > R$ we have $[w(r)]^{-1} > \tau_D$, and the diffusional approach of the reactants is faster than the direct tunnelling mechanism. Hence donors and acceptors separated by a distance $r < R$ disappear by direct tunnelling transfer [described by the term $4/3\pi R^3 N(0)$ in the kinetic equation (37)], and particles for which $r > R$ approach each other to a distance R and then react by the tunnelling mechanism [term $4\pi RDtN(0)$]. Thus the distance $R = \frac{1}{2}a \ln(\nu\tau_D)$ plays the role of a collision diameter in tunnelling reactions involving diffusion of the reactants.

We note from Eqn. (37) that, as predicted[57], the effective initial concentration of donors $n_{eff}(0) = n(0) \cdot \exp[-4/3\pi R^3 N(0)]$, formally determined by extrapolating $\ln[n(t)]$ to $t = 0$, is lower than the real concentration by the number of donors which are initially within a sphere of radius R surrounding the acceptors, and which disappear by diffusionless direct tunnelling within a time τ_D from the beginning of the reaction. The activated nature of diffusion in condensed media is responsible for the monotonic increase of R with decrease of temperature.

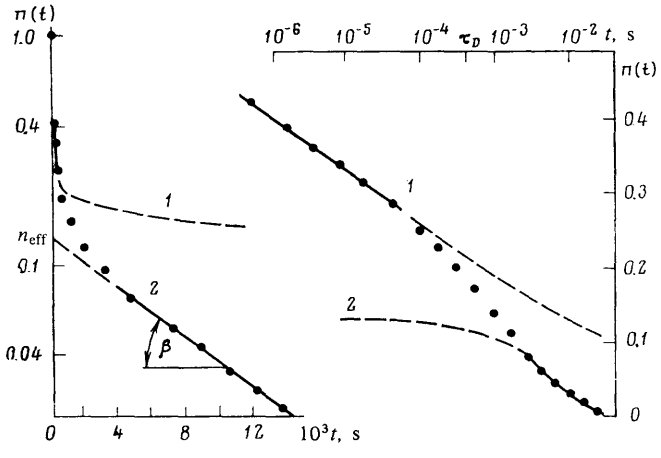


Figure 5. Kinetic curve for the reaction between e^-_{tr} and CrO_4^{2-} (2.5×10^{-2} M) in a 6 M aqueous solution of NaOH at 178 K. The points are experimental, the lines are theoretical curves calculated by Eqn. (26) (curve *1*) and Eqn. (37) (curve *2*) for $R = 31$ Å, $D = 2.2 \times 10^{-12}$ cm^2 s^{-1} ($\tan\beta = 4\pi RDN$).

Miller[33] studied the kinetics of several reactions between e^-_{tr} and acceptors in an aqueous alkaline glass at relatively high temperatures under conditions such that $N(0) \gg n(0)$. By extending his measurements over a wide range of time (from 10^{-6} to 1 s) he was able to observe a change in kinetic law corresponding qualitatively to the transition from a tunnelling ($t \ll \tau_D$) to a diffusion mechanism ($t \gg \tau_D$).

We shall show that these results are described quantitatively by Eqns. (26) and (37). The experimental results[33] are compared in Fig. 5 with calculations by formulae (26) and (37). It can be seen that the initial portion of the kinetic curve is accurately described by formula (26) (curve *1*), whereas the final portion agrees with formula (37) (curve *2*). The numerical values of the diffusion coefficient ($D = 2.2 \times 10^{-12}$ cm^2 s^{-1}) and of the tunnelling distance ($R = 31$ Å) corresponding to curve *2* were obtained by linearising the final portion of the experimental kinetic curve in coordinates of $\ln[n(t)/n(0)]$ against t (Fig. 5). It can be seen from Fig. 5 that the value $\tau_D = a^2/D \simeq 4 \times 10^{-4}$ s corresponds to the transition from the kinetic regime described by Eqn. (26) to that described by Eqn. (37).

In principle the spatial distribution of reactants can alter not only as a result of thermal diffusion but also as a result of tunnelling diffusion through vacancies such as ionised donor particles or empty electron traps (in the case of e^-_{tr}). Kinetic equations for tunnelling reactions under conditions of tunnelling diffusion of electrons have been obtained by Khairutdinov[43], who showed that for short observation times $t \ll J^{-1}$ (where J is the probability of electron transfer by tunnelling diffusion from a donor to a vacancy in unit time), and when the concentration of acceptors in vacancies is much greater than the concentration of donors, the kinetics of the tunnelling reaction are described by Eqn. (26). In the opposite case ($t \gg J^{-1}$) the kinetics are described by an expression analogous to Eqn. (37) in which the quantity $D = \frac{1}{3}R^2/J^{-1}$ plays the role of a diffusion coefficient and R is the distance at which the probability of direct tunnelling recombination between the donor and the acceptor is comparable to the probability of a tunnelling diffusion jump.

An important consequence of that work[43] was the realisation that the kinetic equations for the direct tunnelling transfer of an electron from a donor to an acceptor and for the transfer of an electron by a series of tunnelling jumps into randomly distributed vacancies are quite different. This allows the two mechanisms to be distinguished. For example, the good agreement over a wide range of time between the experimental kinetic curves and those calculated by Eqn. (26) for the reaction of e^-_{tr} with $Cu(en)_2^{2+}$ suggests that this reaction involves direct electron tunnelling rather than the tunnelling diffusion of electrons along traps.

We have reviewed the kinetic equations for tunnelling reactions which can be used directly to analyse existing experimental data. Among the work which has not been discussed we should note a derivation[43] of the kinetic equations for tunnelling reactions under conditions of light-induced electron diffusion and an attempt[40,47,65] to allow for the effect of electrostatic interactions on the tunnelling recombination of charged particles in the presence of diffusion.

V. METHODS OF CALCULATING THE KINETIC CHARACTERISTICS OF TUNNELLING REACTIONS FROM EXPERIMENTAL DATA

The fundamental kinetic characteristics of tunnelling reaction are the parameters a and ν of Eqn. (12) for the probability of tunnelling in unit time. If a and ν are known we can calculate the probability $w(r)$ and the characteristic time $\tau(r) = w^{-1}$ for the tunnelling transfer of an electron to various distances, or the distance R_t to which the electron will tunnel in various times.

The parameters ν and a can be obtained from kinetic data on tunnelling reactions in solids only if the spatial distribution of the reactants is known. This requirement is met by reactions in glassy solutions under conditions such that one of the reactants (say, the acceptor A) was introduced before freezing the solution at a concentration much greater than that of the other reactant (the donor D). By preparing the samples in this way a random distribution of A particles in space can often be achieved[34,66]. It can be seen from Eqn. (26) that under these conditions the spatial distribution of the donors has no effect on the kinetics of the tunnelling reaction.

Kinetic curves are usually obtained by measuring the time dependence of the intensity $I(t)$ of lines in the optical or ESR spectra of the reactant present at lower concentration. The corresponding decrease in the intensity of the spectrum of the second reactant[29] or increase in the intensity of the spectrum of the reaction product[51] can also be monitored. From these measurements we obtain the ratio

$$n(t)/n(t_0) = I(t)/I(t_0),$$

where $n(t)$ is the time-dependent concentration of reactant, and $n(t_0)$ and $I(t_0)$ are the concentration of reactant and the spectral intensity at the beginning of the measurement. However the concentration term in Eqn. (26) is not $n(t_0)$ but $n(0)$, i.e. the concentration at time $t = 0$. Since the concentrations of reactants vary by an approximately logarithmic law in tunnelling reactions, $n(t_0)$ and $n(0)$ can be very different even for very short values of t_0. Direct measurement of $n(0)$ is impossible, and therefore $n(0)$ is usually replaced by the concentration n_c in control samples not containing the second reactant but otherwise identical in every respect with the experimental samples:

$$n(t)/n(0) = n(t)/n_c = I(t)/I_c; \qquad (38)$$

where I_c is the spectral intensity of the control sample. The concentration of particles in the control sample is sometimes found to vary with time as a result of side reactions. In this case the ratio $n(t)/n(0)$ is replaced by $I(t)/I_c(t)$.[50,51]

In kinetic studies of tunnelling processes the reactant whose concentration is monitored is usually generated within the sample by radiolysis or photolysis so as to minimise the possibility of reaction during sample preparation. Under these conditions the assumption $n(0) = n_c$ is legitimate only if the tunnelling reaction between D and A is the only process by which the concentration of D can decrease in the presence of A. However in practice we cannot exclude *a priori* the possibility of a reaction of A with the precursors of D during radiolysis or photolysis. For example, the concentration of trapped electrons could decrease in the presence of acceptors not only as a result of the tunnelling reaction of e^-_{tr} itself, but also through the reaction of A with the precursors of e^-_{tr} (the so-called dry electrons[67]). As a result of such reactions the true initial concentration of donors $n(0)$ in the presence of A can be smaller than n_c (the concentration of D in the control samples not containing A). The quantities $n(0)$ and n_c are related by the expression

$$n(0) = n_c \exp[-\alpha N(0)]. \qquad (39)$$

The parameter α characterises the efficiency with which the precursors of D are captured by the acceptor A. From Eqns. (26), (38), and (39) we obtain

$$I(t)/I_c = n(t)/n_c = \exp\left[-\alpha N - \frac{\pi a^3}{6} N \ln^3(\nu t)\right] \qquad (40)$$

or

$$I(t)/I_c = n(t)/n_c = \exp\left(-\alpha N - \frac{4}{3}\pi R_t^3 N\right). \qquad (41)$$

Thus if $N = N(0)$ is fixed the variation with time of $n(t)/n_c$ is determined by three independent parameters. These parameters can be evaluated by optimising the fit of Eqn. (40) to experimental data. The most obvious criterion of optimum fit is a minimum in the mean-square deviation of the experimental points from the theoretical curve plotted by using Eqn. (40).

Several methods of calculating the optimum values of ν, a, and α have been proposed[58]. In the simplest of these each parameter is varied in turn to give the best linearisation of the experimental kinetic curve in the coordinates which should give a linear plot according to Eqn. (40) or (41).

One of the methods of calculation depends on varying the parameter ν. Eqn. (40) can be written as

$$N^{-1}\ln[n_c/n(t)] = \alpha + (\pi a^3/6)\ln^3(\nu t). \qquad (42)$$

It can be seen from this equation that after choosing the value of ν which gives the most linear kinetic plot of $N^{-1}\ln[n_c/n(t)]$ against $\ln^3(\nu t)$ we can find the best value of a from the slope, which is $\pi a^3/6$, and the best value of α from the intercept on the vertical axis.

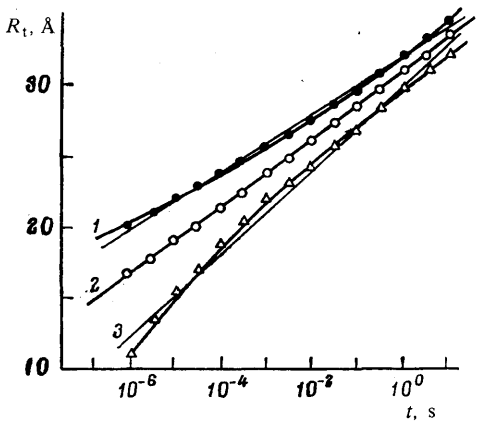


Figure 6. Kinetic plots of R_t against $\ln t$ for the reaction between e^-_{tr} and $K_3Fe(CN)_6$ (0.025 M) in 6 M aqueous NaOH at 77 K: *1*) $\alpha = 0$, *2*) $\alpha = \alpha_{opt} = 8.7\ M^{-1}$, *3*) $\alpha = 2\alpha_{opt}$. Values of R_t calculated by formula (43) from the results of Ref. 33.

In another method of calculation the parameter α is varied. From Eqn. (41) we have

$$R_t = \{(3/4\pi N)[\ln(n_c/n(t)) - \alpha N]\}^{1/3}. \qquad (43)$$

On the other hand, according to Eqn. (17), R_t should vary linearly with the logarithm of time. By choosing the best value of α we optimise the linearity of the experimental kinetic plot of R_t against $\ln t$. As before, the best value of a is obtained from the slope of the resulting straight line, which according to Eqn. (17) is $a/2$, and the best value of ν from the intercept on the vertical axis, which is $(a/2)\ln\nu$ (see Fig. 6).

A detailed analysis of these and other methods of calculating the parameters ν, a, and α can be found in Ref. 58, where it is shown that the results obtained by different methods are acceptably consistent (see, for example, Table 3). However, because of the logarithmic dependence of the concentration of reactants on time, the kinetic measurements must encompass a very wide range of observation times (not less than five orders of magnitude) for a reliable determination of the kinetic parameters of tunnelling reactions.

Table 3. Parameters ν and a calculated[58] by varying $\lg \nu$ (*1*) and α (*2*) from experimental curves for the decay of e_{tr}^- by reactions with different acceptors in aqueous-alkaline glasses at $T = 77$ K.

Acceptor	lg ν, [s⁻¹]		a, Å	
	1	2	1	2
BrO_3^-	11.0	11.2	1.30	1.29
$Co(NH_3)_6^{3+}$	10.9	12.1	2.24	2.05
$Fe(CN)_5NH_3^{2-}$	11.1	10.7	1.65	1.70
MoO_4^{2-}	12.5	11.8	1.41	1.48
$Fe(CN)_6^{3-}$	12.8	13.1	2.10	2.05
$Ni(CN)_4^{2-}$	13.9	13.9	1.31	1.31
IO_3^-	14.1	15.1	1.18	1.12
$Cr(CN)_6^{3-}$	14.9	16.0	2.02	1.92
ReO_4^{2-}	15.2	16.2	1.59	1.51
Np(VII)	15.5	12.9	2.29	2.65
Picrate	15.9	13.5	2.0	2.29
$Co(en)_3^{3+}$	15.7	15.8	1.91	1.90
$Co(CN)_6^{3-}$	17.9	18.4	1.39	1.35
NO_2^-	18.8	19.0	1.03	1.025
$ClAc^-$	20.3	19.6	0.35	0.36
Acrylamide	20.3	22.1	0.72	0.67
NO_3^-	18.6	18.4	0.98	1.02
$Cu(en)_2^{2+}$	15.5	15.0	1.79	1.87
CrO_4^{2-}	19.1	19.1	1.69	1.68

Eqn. (26) assumes that the parameters ν and a are the same for all pairs of reactants. The validity of this assumption has been demonstrated in Ref. 58 for tunnelling reactions in glassy matrices.

VI. KINETIC CHARACTERISTICS OF LONG-RANGE TUNNELLING ELECTRON TRANSFER REACTIONS

The most detailed studies of long-range tunnelling electron transfer are those devoted to the reactions of e_{tr}^- [18,20,29,31-35,57,68-76]. Currently known values of the parameters ν and a for reactions of e_{tr}^- are summarised in Table 3. These values were calculated[58] by analysing experimental data obtained[33,34,58] in kinetic studies of tunnelling reactions of e_{tr}^- extending over a sufficiently wide range of observation times (10^{-6}–10^2 s in Ref. 33 and 34, 10^{-6}–10^6 s in Ref. 58). As Table 3 shows, ν can vary over the very wide range from 10^{11} to 10^{21} s^{-1} depending on the nature of the acceptor, while a varies between 0.4 and 2.5 Å. The ranges of ν and a are very much greater than the experimental error in the determination of these parameters from the kinetic curves (not more than 15%).[58]

Table 4. Parameters ν and a for reactions of particles other than e_{tr}^-.

No.	Donor	Acceptor	Matrix	T, K	lg ν, [s⁻¹]	a, Å	Reference
1	NO_3^{2-}	CrO_4^{2-}	10 *M* NaOH+H_2O	77	20	0.9	77
2	$AgNO_3$	SO_4^-	6 *M* H_2SO_4+H_2O	77	6	1.3	49
3	$FeSO_4$	SO_4^-	ditto	4.2—77	7	1.8	48
4	$K_4Fe(CN)_6$	O^-	6.5 *M* NaOH+H_2O	4.2—77	12	1.8	48
5	$(C_6H_5)_2^-$	$C_{10}H_8$	ethanol + ether	77	7	1.7	50
6	$(C_6H_5)_2^-$	3-phenylethylene 0.01 *M*	ethanol	77	12.5*	1.98*	51
7	$(C_6H_5)_2^-$	3-phenylethylene 0.03 *M*	ethanol	77	13.8*	1.84*	51
8	$C_{10}H_8^+$	CCl_4	ethanol	77—140	—	—	53
9	Cd(I)	$Cr_2O_7^{2-}$	6 *M* H_2SO_4+H_2O	77	12	1.4	55
10	Cd(I)	MnO_4^-	6 *M* H_2SO_4+H_2O	4.2—77	14	1.3	55
11	Ni(I)	MnO_4^-	6 *M* H_2SO_4+H_2O	77	12	1.2	49

*Here $\lg \nu$ and a are the mean values of the parameters calculated[58] by varying $\lg \nu$ and α.

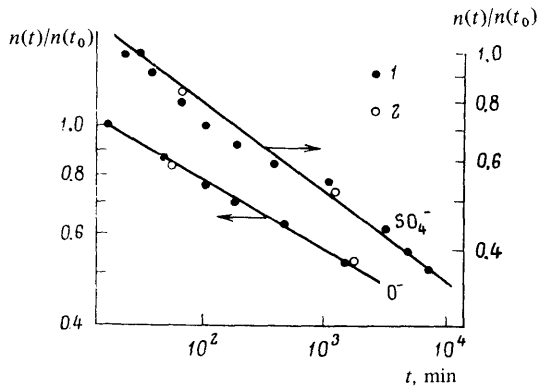


Figure 7. Kinetic plots of $n(t)/n(t_0)$ against $\lg t$ ($t_0 = 10^3$ s) for reactions (6) and (7a) at 77 K (points *1*) and 4.2 K (points *2*). The concentrations of $FeSO_4$ and $K_4[Fe(CN)_6]$ are 0.05 and 0.3 *M* respectively.

An outline of the reactions of particles other than e_{tr}^- is given in Table 4, which lists the kinetic characteristics of these reactions. For processes No. 6 and 7 the values of ν and a were obtained[58] by analysing kinetic curves extending over a wide (10^{-6}–10^2 s) range of time[51]. For the other reactions the kinetic curves were determined over a more limited range of time (not more than three orders of magnitude). As an example we show in Fig. 7 the kinetic curves for reactions (6) and (7a). From data of this type the parameters ν and a can be evaluated only if the parameter α is known from independent measurements[58]. Hence the ν and a values given in Table 4 were obtained by assuming $\alpha = 0$ (except in the case of processes No. 6 and 7). These values, therefore, are an upper limit of the true value of ν and a lower limit of the true value of a.[58] As Table 4 shows, the range over which the parameters ν and a can vary in the different reactions is similar to the range of variation of these parameters for the reactions of e_{tr}^-.

We should note also that the values of ν and a (Tables 3 and 4) agree well with theoretical calculations[58] (see Chapter III).

Table 5. Temperature dependence of the parameters ν and a for the reactions between e^-_{tr} and various acceptors, calculated[58] from kinetic data[33] by varying $\lg \nu$ (*1*) and α (*2*).

Acceptor	T, K	$\lg \nu$, $[s^{-1}]$		a, Å	
		1	*2*	*1*	*2*
$Co(en)_3^{3+}$	77	15.7	15.8	1.91	1.90
$Co(en)_3^{3+}$	143	11.1	13.1	2.5	2.2
CrO_4^{2-}	77	19.1	19.1	1.69	1.68
CrO_4^{2-}	147	10.0	10.9	2.97	2.74
NO_3^-	77	18.6	18.4	0.98	1.02
NO_3^-	143	10.6	10,6	1.69	1.49
BrO_3^-	77	11.0	11.2	1.30	1.29
BrO_3^-	143	13.0	11.5	1.02	1.13

The few data so far available on the temperature dependence of the parameters ν and a are summarised in Table 5. It can be seen that at least for the reactions of e^-_{tr} with CrO_4^{2-} and NO_3^- the parameter a increases very significantly with temperature. One possibility is that in these cases a new reaction path becomes available on raising the temperature, involving the excited electronic levels of the reaction products. In parallel with an increase of a we observe a decrease of ν, but overall the velocity of the reaction increases with temperature. On the other hand the variation of ν and a for the reaction of e^-_{tr} with BrO_3^- lies within experimental error, and for the reaction of e^-_{tr} with $Co(en)_3^{3+}$ is close to the limits of experimental error.

Conversely, the rate of the reaction of e^-_{tr} with biphenyl in 2-MTHF[78] and with benzyl chloride in C_2H_5OH [79] apparently increases as the temperature is lowered. As shown in the original papers, the influence of the acceptors on the radiation yield of e^-_{tr} decreases as the temperature increases from 4.2 to 77 K.

Thus the range of ν values in these tunnelling reactions extends from 10^6 to 10^{21} s^{-1}, and the range of a values extends from 0.4 to 2.5 Å. Both parameters depend on the nature of the electron donor and the electron acceptor, and they can decrease, increase, or stay constant when the temperature is increased. All these experimental findings are fully consistent with the theoretical model of long-range tunnelling electron transfer proposed in Ref. 58.

VII. CHEMICAL REACTIONS INVOLVING LONG-RANGE ELECTRON TRANSFER

Electron transfer reactions play an important rolé in various chemical situations. Many redox reactions in liquids or on solid surfaces, and also many electrochemical, radiation-chemical, photochemical, and biochemical changes include an electron transfer step.

The long-range electron transfer reaction allows chemical change to take place when the reactants are separated by a relatively large distance, thus offering interesting new possibilities in the organisation of chemical changes at the molecular level and in the control of these changes. These possibilities are fully utilised in the living world, for example in respiration and in photosynthesis[80]. The substances which take part in these complex biochemical processes are often immobilised in membranes, thus being prevented from undergoing undesirable side-reactions by collision processes. Nonetheless these substances can exchange electrons by a tunnelling mechanism[22,23,59,60,81-89]. The resulting oxidised and reduced forms can initiate chains of chemical reactions within their own region of the membrane.

We may assume that natural photosynthetic systems are able, by virtue of this type of organisation of chemical changes, to avoid fast recombination of the electrical charge pairs produced by the absorbed radiation, thus ensuring efficient photosynthesis. Separation of charges probably occurs by fast tunnelling electron transfer from the photo-excited chlorophyll (Chl) to the so-called primary acceptor (A):

$$Chl \xrightarrow{h\nu} Chl^* \xrightarrow{A} Chl^+ + A^-.$$

The species Chl^+ and A^- initiate further chemical changes, leading ultimately to the evolution of oxygen from water and to the formation of carbohydrates from CO_2. The reverse electron transfer from A^- to Chl^+ is much slower. A possible explanation is the rapid conversion into heat of some of the energy stored in Chl^+ and A^- (the conditions which favour tunnelling electron transfer may be disturbed by lowering the energy levels); alternatively, the separation of the reactants may be increased by fast conformational changes in the membrane produced by the forward reaction. The fast recombination of light-separated charges is known to be the major obstacle to the design of artificial solar energy converters. By analogy with natural photosynthesis, the use of tunnelling processes would seem a promising way of overcoming these difficulties.

Table 6. Rate constants k_e for the reactions of e^-_{tr} with various acceptors in liquid solutions at 25° C and characteristic times τ for the reactions of e^-_{tr} with the same acceptors in solid aqueous-alkaline glasses at 77 K.

Acceptor	$10^{-10}k_e$, litre mole^{-1} s^{-1}	τ, s		
		R=10 Å	R=15 Å	R=20 Å
$ClAc^-$	0.12	$10^{4,6}$	10^{17}	—
NO_3^-	0.85	$10^{-9,9}$	$10^{-5,6}$	$10^{-1,3}$
$Cu(en)_2^{2+}$	1.8	10^{-10}	$10^{-7,5}$	10^{-5}

Tunnelling processes can be used to control the selectivity of redox reactions. This has not yet been achieved in practically important situations, however the possibility (in principle) of this type of control is shown by Table 6, in which we compare the rate constants for the reactions of hydrated electrons with three different acceptors in a liquid at 25° C and the characteristic times τ for the reactions of trapped electrons with the same acceptors in solid aqueous alkaline glasses at 77 K. It can be seen that in liquids, where the reactants can approach each other by diffusion (direct collisions), the rate constants for all three reactions are similar and very large. On the other hand in solids, where diffusion is negligible and the reactions

take place by a tunnel mechanism, the characteristic times of the reactions vary with distance to different extents because of the differences in ν and a. For the reaction of e_{tr}^- with $Cu(en)_2^{2+}$ we obtain $\tau = 10^{-5}$ s even for $R = 20$ Å, and $\tau = 10^{-10}$ s for $R = 10$ Å. On the other hand the τ value for the reaction of e_{tr}^- with $ClAc^-$ is 14–15 orders of magnitude greater with $R = 10$ Å. This difference in the distance dependence of the time τ suggests the possibility of exploiting the tunnel effect for generating selectivity in redox reactions by creating barriers against direct collisions between the reactants. The gain in selectivity would be achieved at the cost of a loss in speed, but this could be unimportant in many fast electron transfer processes.

In solids there is practically no possibility of direct collisions between the reactants, and therefore the distance of the tunnelling transition (and hence the time τ) can be controlled by controlling the concentration of the reactants. In the case of liquids close approach between the reactants could be prevented by surrounding them with a shell of inert molecules (large ligands, or micelles). Experimental confirmation of the differences in tunnelling electron transfer behaviour between particles inside and outside a micelle has recently been obtained[90,91].

Long-range tunnelling electron transfer processes play an important role in radiation chemistry and in photochemistry. They enable many oxidation–reduction reactions in irradiated solid matrices to take place at rates well in excess of the diffusion-limited rate.[57] The tunnelling recombination of positive and negative ions can set a limit to the steady-state concentration of these particles in radiolysis[21], and it can produce time-changes in the radiation-chemical yield[57].

Long-range electron transfer can be important also in the protection of materials from radiation damage and photo-degradation[92,57]. By using the tunnel mechanism the photochemical changes of some organic materials in solids can be made to occur by a one-photon rather than a two-photon process, i.e. with a smaller energy input[52].

Tunnelling electron transfer is very relevant also in oxidation–reduction catalysis, including enzyme reactions. Thus it has been shown[93] that the two-electron reduction of molecular oxygen to hydrogen peroxide by Cu^+ ions immobilised in blue (copper-containing) oxidases is thermodynamically unfavourable. Hence we may assume that molecular oxygen is reduced directly to water when complexed with the active centres of these enzymes[94]:

$$4Cu^+ + O_2 + 4H^+ \rightarrow 4Cu^{2+} + 2H_2O.$$

It appears that two electrons are transferred from copper ions directly bound to oxygen in the complex, and two additional electrons are transferred from more remote copper ions in the enzyme molecule.

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