CHARGE TRANSFER REACTIONS ACCOMPANIED BY A CHANGE IN THE COORDINATE OF A HEAVY PARTICLE

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UDC 541.13

The characteristic features of the course of the elementary act of a charge transfer reaction, associated with a change in the coordinate of a heavy discharging particle, are examined. The concept of quasi-barrierless (and quasi-activationless) processes is introduced; these processes are distinguished by the fact that the reaction path along the solvent coordinate is barrierless (or activationless, respectively), whereas the total energy surface with allowance for the coordinate of the ion includes a potential barrier. The regular kinetic features of quasi-barrierless processes are analogous to those for true barrierless reactions. At the same time the existence of a barrier is responsible for retardation of the back reaction and preservation of first order with respect to the discharging ion for the quasi-barrierless process. When allowance is made for the excitation of intermolecular vibrations it is found that for any reactions of charge transfer the transfer coefficient α practically never exceeds unity. Schemes for the elementary act in various types of electrode reaction – the oxidation of anions to free elements, the deposition of metals from simple ions, redox reactions, and reactions involving the rupture of a covalent bond – have been examined qualitatively.

In recent years the idea that the activation process in an electrode reaction (and in general for a reaction of charge transfer) is associated essentially with reorganization of the solvent, and a change in its polarization, has been widely accepted. This idea, which originated in qualitative form in papers by Gurney [1, 2], was developed quantitatively in papers by Marcus and more particularly Levich, Dogonadze, and coworkers (for a review see [3]). Until recently this theory was applied only to redox reactions taking place without change in the coordinate of the reacting particle – the only variable was the coordinate effectively describing the polarization of the solvent. Recently, Dogonadze, Kuznetsov, and Levich [4, 5] also examined reactions involving transfer of a proton, i.e., involving the rupture and formation of covalent bonds. In a sense, however, this treatment is analogous to the theory of redox reactions – the activation process is due exclusively to the thermal motion of the molecules of the solvent, and when the appropriate configuration of the solvent is attained, quantum jump-over of an electron or a proton (or both) from one state to another takes place. As a rule, only the ground energy levels of the two states play a significant role in the process.*

It is worthwhile to qualitatively examine reactions accompanied by a significant change in the coordinate of a heavy reacting particle. A typical example of a reaction of this kind is the process of anodic liberation of chlorine, where in the discharge act the Cl^- ion, which has a radius of 1.8 Å, is converted into an adsorbed Cl atom with a covalent radius of about 1.0 Å. Thus, during the elementary act a marked displacement of the heavy nucleus of the chlorine is unavoidable, and this should be taken into account in a description of processes of this type [6].

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* Excited levels make the main contribution in the range of barrierless and activationless reactions.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 6, No. 4, pp. 507-515, April, 1970. Original article submitted March 20, 1969.

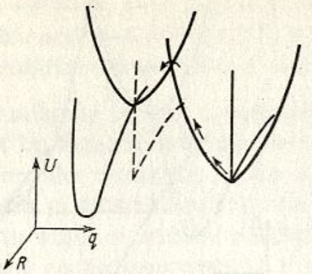

Fig. 1

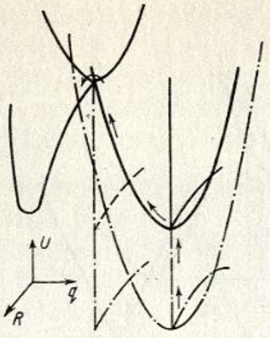

Fig. 2

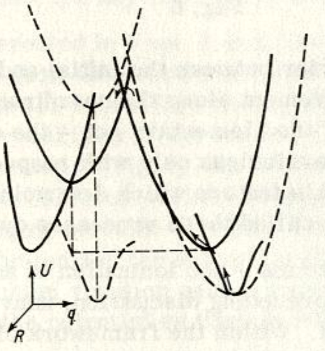

Fig. 3

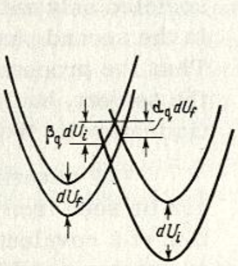

Fig. 4

It is most straightforward to consider a process in which it is assumed that the discharging ion is incompressible. The dependence of the energy of the system on the ion-electrode distance will then be described by a curve of the type shown on the right of Fig. 1 – the potential well for the chloride ion is bounded on the electrode side by a vertical straight line. The potential curve for the adsorbed chlorine atom is shown on the left and is of the usual type. For clarity, a projection of the curve for the ion is shown in the same plane. The point of intersection of the potential curve of the atom and the projection of the curve for the ion corresponds to the state into which the system would move as a result of discharge of the ion if the discharge process were not associated with a change in the state of the solvent. In fact, however, the solvent must undergo reorganization. The process of its reorganization accords with the dependence of the energy on the coordinate.* On the whole, the most favorable reaction path involves the reorganization of the solvent without change in coordinate of the chlorine nucleus, followed, when the point of intersection of the curves for the initial and original states is reached, by jump-over of the electron and the formation of an adsorbed atom with a greatly elongated covalent bond and subsequent dissipation of energy in the process of establishment of the equilibrium of the chlorine atom and the equilibrium polarization of the solvent.†

When the level of the original state is sufficiently low, we may have the situation represented by the continuous curve in Fig. 2. In this case the activation phase, which is due to the change in the state of the solvent, is not associated with the surmounting of a potential barrier – the activation energy is equal to the difference in the energies of the system at the start and at the end of this phase (but not of the elementary act as a whole !). Since the kinetics are influenced directly by the magnitude of the activation energy, a reaction of this type will obey all the regular features of barrierless processes [7]; in particular, the transfer coefficient $\alpha = 1$. Strictly speaking, however, this process is not barrierless: as can be seen from

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* In Fig. 1, to simplify the drawing, we have drawn the curves $U = U(R)$ and $U = U(q)$, which are vertical sections of the mutually perpendicular planes of the surfaces $U(R, q)$. These surfaces are readily constructed by moving the minima of the $U = U(q)$ curves along the curves $U = U(R)$.

†In the energy dissipation phase the system does not necessarily descend along the curves shown in Fig. 1, but descends by any path on the corresponding energy surface.

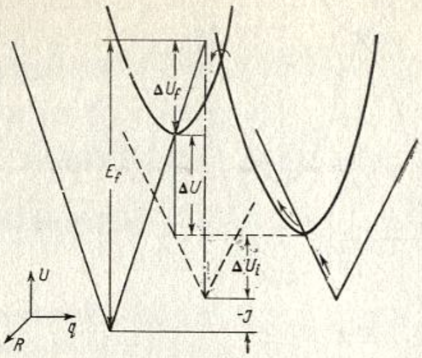

Fig. 5

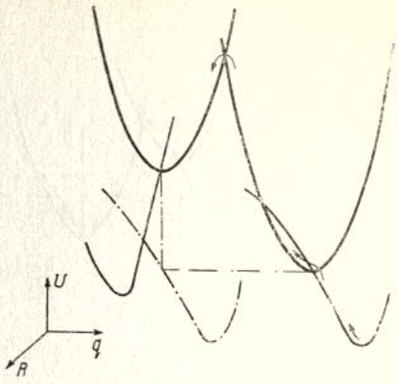

Fig. 6

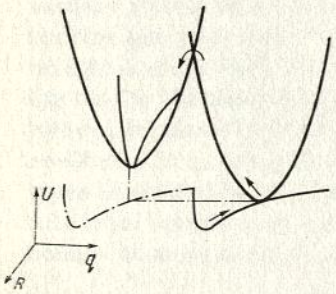

Fig. 7

Fig. 2, there is a barrier between the initial and final states, but it is associated only with movement along the coordinate of the chlorine nucleus in the second phase of the elementary act – the dissipation of energy. Thus the process is barrierless only with respect to the coordinate of the solvent, but it is this feature which determines its basic regular kinetic features. We have called these processes quasi-barrierless [6]. *

The reverse reaction – the ionization of adsorbed chlorine – as can be seen from the preceding discussion, unavoidably involves elongation of a covalent bond. Within the framework of this model (the ion is an incompressible sphere) this elongation takes place at all potentials up to the same distance and requires a certain constant expenditure of energy. When the discharge is quasi-barrierless, the ionization can be described as quasi-activationless – its activation energy is not equal to zero, but it does not depend on the potential ($\beta = 0$), since activation does not take place along the coordinate of the solvent.

We previously pointed out [6, 9] that experimental observation of a barrierless process is possible only when the product of the barrierless discharge, as a result of some subsequent process, is rapidly converted into another, relatively stable particle. In fact, if this were not the case, almost the entire product of the barrierless discharge would be immediately converted reversibly into the original substance as a result of the extremely rapid activationless ionization. In particular, for the barrierless discharge of hydrogen ions, this second stage, competing with the activationless ionization, is activationless electrochemical desorption [9].

For quasi-barrierless processes, an activationless second stage in this sense is not necessary – its role is played by the second phase of the quasi-barrierless reaction – for the rapid change in the coordinate of the reacting particle, as a result of which it enters a new potential well and cannot now return to the original state at a very high rate. In other words, since in the quasi-barrierless process the activation energy of the back reaction is not equal to zero, it does not necessarily take place so rapidly that it masks the barrierless process. It is the quasi-barrierless nature of the process which makes it possible to explain the first order of the reaction with respect to chloride ion in the range $\alpha = 1$ [6].

Allowance for the coordinate of the discharging particle makes it possible to examine another interesting problem associated with the theory of barrierless transitions. Let us consider the case represented by the dot-dash line in Fig. 2, i.e., the difference in energies is so great that the term (with respect to the solvent) of the final state is inside the term of the initial state. For this arrangement of the curves, the change in the activation energy with potential should have been greater than the change in the heat of the elementary act, i.e., $\alpha > 1$, but this was not observed experimentally. An explanation for this for any electrode process was given by Dogonadze, Kuznetsov, and Levich [4, 5]: the most readily understood process involves the shift from higher electron levels of the metal – the expenditure of energy for the excitation of electrons in the

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* Similar considerations were put forward almost simultaneously by Kuznetsov [8].

initial state (the continuous curve in Fig. 2 corresponds to this state, excited relative to the lower curve) is more than compensated by the decrease in the energy used up in the reorganization of the solvent. For reactions in the bulk of a solution, this explanation is of course inapplicable. For volume processes of proton transfer, Dogonadze and co-workers [10] took into account the possibility of excitation of proton levels; in this case calculation shows that α is not significantly greater than unity.

It follows from the scheme in Fig. 2 that for any volume reactions, and not only reactions involving proton transfer, α cannot be significantly greater than unity. In fact, there is always the possibility of a displacement upwards from the minimum of the dot-dash curve to the minimum of the continuous curve as a result of the excitation of intermolecular vibrations along the coordinate R (the distance from the reacting particle to that with which it will be combined in the final state), and then reorganization of the solvent in accordance with the continuous curve. With change in the heat of the reaction (displacement of the dot-dash curve) there will be a change of equal magnitude in the energy used up in the excitation of the intermolecular vibrations, and the contribution of the reorganization of the solvent to the activation energy will remain constant. Thus, for any reations of charge transfer in solution, the limiting value of $\alpha = 1$.*

The schemes represented in Figs. 1 and 2 relate to the model in which the ion is regarded as an incompressible sphere. In fact, ions exhibit a certain compressibility, so that the vertical straight line in the potential curve for the ion should be replaced by a smooth curve, whose curvature increases rapidly, however, since the compressibility of the ion is still extremely small. Quantitatively, the picture should be similar to that represented in Fig. 3. An interesting feature is that now a more favorable reaction path may might be that which was considered earlier (change in the coordinate of the solvent without change in the coordinate of the discharging particle — broken line in Fig. 3), but activation associated with a change in the coordinates of both the ion and the solvent (e.g., along the path indicated by the arrows along the continuous curve). The optimum reaction path is found from the condition for the minimum activation energy (i.e., the saddle point of the potential surface is found).

Let us move from the optimum coordinate R^* upwards along the $U_i(R)$ curve by an amount of $dU_i(R)$ (Fig. 4). There is then added to the activation energy a quantity $dU_i(R)$ (since the activation energy is read from the minimum of the $U_i(R)$ curve), but there is a simultaneous decrease by an amount of $\alpha_q dU_i(R)$ in the energy of activation along the coordinate of the solvent, since we have raised the minimum of the U(q) curve for the initial state by $dU_i(R)$ (the quantity α_q is the transfer coefficient for the terms of the solvent, determined in the usual way from the ratio of the slopes of the U(q) curves for the initial and final states at the point of intersection). The change in the coordinate R leads not only to a raising of the minimum of the U(q) curve of the original state by $dU_i(R)$, but also to a lowering of the minimum of the U(q) curve for the final state by a quantity of $dU_f(R)$. The values of $dU_f(R)$ and $dU_i(R)$ are related to one another as the corresponding slopes of the curves, i.e., $dU_f(R) = (\beta_R/\alpha_R)dU_i(R)$ (α_R and $\beta_R = 1 - \alpha_R$ are the transfer coefficients, determined by the ratio of the slopes of the $U_i(R)$ and $U_f(R)$ curves). The lowering of the final term of U(q) leads to a decrease in the activation energy by $\alpha_q dU_f(R) = \alpha_q(\beta_R/\alpha_R)dU_i(R)$. The total change $dA = dU_i(R) - \alpha_q dU_i(R) - \alpha_q(\beta_R/\alpha_R)dU_i(R)$. From the definition of the minimum† $dA/dU_i(R) = 1 - \alpha_q - \alpha_q(1 - \alpha_R)/\alpha_R = 0$, from which $\alpha_q = \alpha_R$.

If the minimum of the $U_i(R)$ curve is moved by an amount dQ, e.g., as a result of a change in potential, the point of the optimum transition is also, generally speaking, moved simultaneously by an amount dR. The total change in the activation energy is $dA - \alpha_q \alpha Q + dU_i(R) - \alpha_q dU_i(R) - \alpha_q dU_f(R)$. Since at the point of the optimum transition $\alpha_q = \alpha_R$, we obtain $dA/d\alpha = -\alpha = -\alpha_q = -\alpha_R$, i.e., the measured transfer coefficient is equal to that for the U(q) and U(R) curves. The optimum transition takes place at the point at which α_q and α_R become equal. The nature of the dependence of α on the difference in the levels of the initial and final states is determined in the general case by the form of the U(q) and U(R) curves, a greater contribution being made by one of these curves, depending on the specific form of the corresponding functions.

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* If account is taken of the quantization of intermolecular vibrations, it can be shown that under certain conditions α may be slightly greater than unity; the deviations from unity are greater, the greater the distance between the vibrational levels.

†In addition to the extremum condition that the first derivative be equal to zero, the minimum also requires the condition $\frac{d^2A}{dU_i(R)^2} = \frac{1}{\alpha_R}\left(\frac{d\beta_q}{dU_i(R)} - \frac{\alpha_q}{\alpha_R}\frac{d\beta_R}{dU_i(R)}\right) > 0$, which at the extremal point is equivalent to the condition $d\beta_q/dU_i(R) > d\beta_R/dU_i(R)$ — an inequality which in principle may not be satisfied, although it is observed in the model examined below (and in various other models).

The realization of the version described above is not always possible – in some cases the optimum coordinate R determined in this way is found to be physically unreal and the activation takes place without change in the coordinate of the ion. It is convenient to clarify this by examination of a specific model.

Let us imagine (Fig. 5) that U(q) is given by a parabola, as is usually assumed for a process involving the reorganization of a solvent [3], and that the function U(R) can be represented in the form of straight lines with different slopes.* The energy of activation for a certain arbitrary path A is equal to $\Delta U_i + A_q$, where ΔU_i is the displacement upwards along the $U_i(R)$ curve from its minimum, and A_q is the energy of activation with respect to the term of the solvent, i.e., the difference in the energies at the minimum of the initial U(q) curve and at the point of its intersection with the final U(q). It can readily be shown [3] that this quantity $A_q = (E_s + \Delta U)^2/(4E_s)$, where E_s is the energy of reorganization of the solvent (the change in U(q) with change in q from the equilibrium value for the initial state to the equilibrium value for the final state), and ΔU is the difference in the energies of the minima of the U(q) curves. It can be seen from Fig. 5 that $\Delta U = J + E_f - \Delta U_i - \Delta U_f$, where J is the difference in the equilibrium energies of the initial and final states (the difference in the minima of $U_i(R)$ and $U_f(R)$ with change in R from the equilibrium final value of the equilibrium initial value, and ΔU_f is the change in $U_f(R)$ for the change in R corresponding to ΔU_i. $\Delta U_f = (\beta_R/\alpha_R)\Delta U_i$, and for linear terms the ratio β_R/α_R is constant. By substituting these relationships in the expression for A and equating $dA/d\Delta U_i$ to zero, we obtain the optimum value $\Delta U_i^* = \alpha_R[(\beta_R - \alpha_R)E_s + J + E_f]$, corresponding to the activation energy $A^* = \alpha_R(\beta_R E_s + J + E_f)$ and the transfer coefficient $dA/dJ = \alpha = \alpha_R$.

The latter is independent of J (in contrast to the case where the terms are nonlinear) and is determined entirely by the ratio of the slopes of the straight lines $U_i(R)$ and $U_f(R)$. As shown above, at the optimum point $\alpha_q = \alpha_R$, i.e., throughout the entire range J in which the relationships derived above are applicable, the intersection of the U(q) curves takes place at the same point and their mutual disposition remains unchanged.†

This solution is obviously meaningful only in the case where R* lies between the equilibrium coordinates R_i and R_f, i.e., if $\Delta U_i^* > 0$ and $\Delta U_f^* < E_f$, and also if $|\Delta U| \leq E_s$ (otherwise, the branches of the potential curves with the same sign for the derivative intersect and the initial equations should be different). The last condition is satisfied for $1 > \alpha > 0$, i.e., throughout the entire range of normal discharge.‡ The first conditions are fulfilled for $(\alpha_R - \beta_R)E_s - E_f < J < (\alpha_R - \beta_R)E_s + (\alpha_R/\beta_R)E_f$. If J lies outside this range, we find that activation takes place for $\alpha = \alpha_q \neq \alpha_R$ for unchanged R corresponding to the equilibrium coordinate of the initial state (the left-hand inequality is not observed), or with change in R to the final equilibrium value.

The description of the terms by means of straight lines is of course an approximation which is applicable only for individual sections of the potential curves. It is clear that as the ion approaches the electrode, the forces of repulsion increase to such an extent that the potential curve can be replaced by an almost vertical straight line. In this case, all the arguments which were put forward at the start of this paper become applicable. It appears extremely probable that within a certain range J the activation takes place with a change in the coordinate R until the transition coordinate moves into the range of sharp increase in $U_i(R)$, after which R remains unchanged.**

The above discussion presupposes the possibility of continuous movement of the system along the coordinate R. It is of interest to estimate the extent to which this assumption is justified. The form of the potential well for the ion close to the electrode, in a first approximation at least, will be determined by the action of image forces and forces of repulsion. These effects are of the same order as those in ionic mole-

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*The picture remains essentially unchanged if a straight line describes with a good degree of approximation the behavior of the true U(R) curve over a sufficiently wide range of values of U.

†The fact that ΔU for the optimum path is independent of J for the given model can be readily demonstrated by direct calculation: $\Delta U^* = J + E_f - \Delta U_i^* - \Delta U_f^* = J + E_f - (1/\alpha_R)\Delta U_i^* = (\alpha_R - \beta_R)E_s$.

‡The term "normal" used in [4] appears to us more appopriate than the term "ordinary" which we previously used [7].

**It may be noted that the process involving change in R and q does not necessarily take place along the curves represented in the figures given above with a change first in R and then q. The same result may be obtained by moving from the initial point to the apex of the activation ridge by other paths over the appropriate energy surface.

cules – alkali metal halides formed by the vapors of ions with similar radii. Comparison with the corresponding quantities [11] (with allowance for the increase in the reduced mass on going from the binary molecule to the electrode – ion system) shows that the vibrational quanta for the halogens amount to approximately 0.5-1.5 kT, i.e., the classical treatment of the process is possible, at least for the largest ions. For the fluoride ion, however, and probably also for the chloride ion, the quantum-mechanical approach is necessary. The quantum character of the motion has a significant influence for any ions with significant increase in the distance from the equilibrium position, since here we can expect the potential curve to rise extremely sharply. The quantitative treatment of the scheme with an incompressible ion (Figs. 1 and 2) should be a quantum treatment.

If the distance between the vibrational levels of the ion is significantly greater than kT, we cannot continuously alter the coordinate of the point for the most favorable transition. Excitation of the vibrations of the ion becomes unlikely, and the chief activation path is that involving reorganization of the solvent without change in the state of the ion, i.e., the picture will be analogous to that examined above for the incompressible sphere model.

As shown in [10] for the intramolecular vibrations of a proton, in the range of normal discharge the excited vibrational levels for the most part do not take part in the process, but as the range of barrierless discharge is approached, the transition from excited levels becomes more favorable, until it becomes the main reaction path. The increase in the role of the excited levels influences the nature of the dependence of α on J – the change from $\alpha \simeq 1/2$ to $\alpha \simeq 1$ takes place more sharply than might have been expected merely on the basis of the form of the U(q) curves.

Qualitatively, the same picture should be expected for the excitation of intermolecular vibrations (ion – electrode vibrations). As noted above, in the range of the barrierless discharge the chief reaction path is the transition through the excited vibrational states of the original ion, whereas in the normal range the participation of excited levels is unlikely. It is natural that in the transitional range the role of the excited levels increases. The transition from $\alpha \simeq 1/2$ to $\alpha \simeq 1$ becomes correspondingly sharper. A quantitative analysis of the problem naturally requires refinement of the characteristics of the terms of U(R).

The example considered above involving the discharge of Cl^- ions is apparently typical for most reactions involving the oxidation of comparatively simple anions, since it is known that for all nonmetals the radii of the anions are greater by 0.7-0.9 Å than the covalent radii of the atoms [12], i.e., the discharge process should involve significant approach of the corresponding atom to the electrode.

The opposite relationships apply for the reduction of metal cations: the metallic radius is 0.7-1.0 Å greater than the ionic radius [12],* so that during the elementary act, the distance between the nucleus of the discharging ion and the metal increases. A scheme for this process is illustrated in Fig. 6. In this case the activation is associated with preliminary excitation of the vibrations of the ion.

To the extent that the vibration of the ion in the direction away from the electrode is associated with its diffusion into the solution, the potential curve in this direction cannot rise too steeply and too high, and we can here speak only of a slight ridge of order of magnitude not greater than the activation energy of diffusion. Thus, this process does not make a marked contribution to the activation energy of discharge, and the overall picture will probably be determined by the reorganization of the solvent.

For inorganic redox reactions, the effects due to intermolecular vibrations are also apparently small, since the radii of ions with variable valence as a rule change by only 0.1-0.15 Å (or very rarely by up to 0.2 Å) with change in the charge by unity [12]. In principle, however, they cannot be neglected, particularly as regards the role which they play in quasi-barrierless transitions. In redox reactions involving the rupture of a chemical bond (organic reactions, the reduction of hydrogen peroxide, etc.), two paths are possible. The first involves the primary formation of a relatively stable radical-ion, which subsequently decomposes with bond rupture. To the extent that the interatomic distances in radical-ions are fairly close to those in neutral molecules (and to the extent that the excitation of the corresponding intramolecular bonds usually requires large quanta and therefore has a low probability), this reaction path is followed with practically no change in the intramolecular coordinates and is analogous to ordinary redox processes.

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*We shall consider only the ions of nontransition metals, which do not form strong coordinate bonds with the solvent molecules. For transition metals, however, it is actually a complex ion which undergoes discharge.

The other reaction path involves bond rupture during the actual elementary act with the immediate formation of two particles – an ion and a radical. This path may be preferred, if the formation of the radical-ion is energetically unfavorable. The van der Waals radius of the atom is usually approximately equal to the radius of the corresponding singly-charged anion and is greater by ~0.8 Å than the covalent radius [13]. The radius of the cation is smaller by approximately the same amount. Thus when bond rupture is accompanied by the formation of a radical and a cation (oxidation), the distance between the atoms may change little, but if a radical and an anion are formed (reduction), the interatomic distance during the elementary act should increase by approximately 1.5 Å.*

A scheme for this process is represented in Fig. 7, in which R denotes the distance between the atoms of the bond being broken (the distance from the molecule being reduced to the electrode, in accordance with the above considerations, is assumed to be practically constant). Here an important feature is that the $U_f(R)$ curve for the final state, corresponding to the repulsion between the ion and the radical, rises extremely steeply, whereas the $U_i(R)$ curve is fairly flat in the range of marked elongation of the bond. Since with marked increase in the distance from the equilibrium position the anharmonicity of the vibrations has a significant influence, the distances between the vibrational levels decrease considerably and may become much less than kT, so that in this range the movement of the system can be described by the classical approximation.† We can then apply to this process the model considered above, in which the corresponding sections of the U(R) curves are replaced by straight lines. Since for this model the measured value of α is determined by the ratio of the slopes of the straight lines, whereas for the final state $U_f(R)$ rises much more steeply, a result should be values of α significantly less than 1/2. It is possible that it is this feature which is responsible for the value of α equal to about 0.25 observed in the cathodic reduction of hydrogen peroxide [14].

The author thanks R. R. Dogonadze and A. M. Kuznetsov for interesting discussion of problems relating to the subject of the present paper.

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*A slightly smaller effect is possible, since the van der Walls radius of an atom with unsaturated valence may be less than that in the normal case, but it is clear that we are still dealing with an increase in distance by a quantity of the order of 1 Å or more.

†For example, for the H_2O_2 molecule, estimation for the vibrations along the O – O bond on the basis of data on the F_2 molecule, which is close in the parameter series [11], shows that for elongation of the bond by 1 Å the distance between the levels is of the order of 0.2 kT.