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ELECTRON TRANSFER AT ELECTRODES AND IN SOLUTION: COMPARISON OF THEORY AND EXPERIMENT*

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Abstract—Detailed quantitative information about different theoretical aspects of electron-transfer rates in solution and at electrodes can be obtained from appropriate experiments. Recent theoretical work has predicted certain quantitative correlations between rates of crossed-redox reactions and rates of isotopic exchange, and between homogeneous and electrochemical rates. Experimental tests of these predictions yield insight into "intrinsic" and "driving force" factors.

The intrinsic factor is related to differences in properties of oxidized and reduced species (*eg*, differences in corresponding bond lengths and differences in solvent orientation polarization). The driving force term is related to the standard free energy of reaction in the homogeneous reaction and to the activation overpotential in the electrode reaction.

Measurements of temperature coefficients of rates in dilute solution provide some information about adiabatic and dielectric-saturation effects. Absolute rates, in conjunction with knowledge of bond-length differences and bond-force constants, provide some insight into the over-all picture, (instrinsic, adiabatic, unsaturation factors *etc*). Study of the cited quantitative correlations permits the cancellation of many effects, and so can reveal others.

The present state of experimental information on these theoretical topics is described.

Résumé—Des informations quantitatives détaillées concernant différents aspects théoriques des vitesses de transfert d'électron en solution et aux électrodes ont été obtenues au moyen d'expériences appropriées. Un travail théorique récent a prédit des corrélations quantitatives certaines entre vitesses de réactions redox croisées et vitesses d'échange isotopique, de même qu'entre vitesses réactionnelles homogènes et électrochimiques. Les tests expérimentaux de ces prédictions donnent une idée des facteurs "intrinsèque" et "force motrice".

Le facteur intrinsèque est relié aux différences de propriétés des espèces oxydées et réduites (par exemple différences dans les longeurs de liaison correspondantes et différences dans l'orientation de polarisation du solvant). Le terme de force motrice est rapporté à l'énergie libre standard de la réaction, pour la réaction homogène et à la surtension d'activation pour la réaction d'électrode.

Des mesures de coefficients de température des vitesses en solutions diluées apportent quelque information sur les effets de saturation adiabatique et diélectrique. Les vitesses absolues, conjointement à la connaissance des différences de longeur de liaison et des constantes de force de liaison, fournissent quelques éclaircissements sur le phénomène global, (intrinsèque, adiabatique, insaturation facteurs *etc*. . . .)

On rend compte de l'état actuel de l'information expérimentale sur de tels sujets théoriques.

Zusammenfassung—Geeignete Experimente liefern detaillierte, quantitative Informationen über verschiedene theoretische Aspekte bezüglich der Geschwindigkeit der Elektronenübertragung in Lösungen und an Elektroden. Eine neuere theoretische Arbeit hat gewisse quantitative Beziehungen zwischen den Geschwindigkeiten gekreuzter Redoxreaktionen und Isotopenaustauschreaktionen einerseits, sowie zwischen den Geschwindigkeiten homogener und elektrochemischer Reaktionen andererseits vorausgesagt. Experimentelle Untersuchungen dieser Voraussagen geben Aufschluss über "systemgebunde" und "energetische" Faktoren.

Der systemgebundene Faktor ist mit den Unterschieden in den Eigenschaften der oxydierten und reduzierten Teilchen (z.B. Unterschiede in den entsprechenden Bindungslängen und Unterschiede in der durch die Lösungsmittel-Orientierung verursachten Polarisation) verknüpft. Der energetische Term steht in Beziehung zur freien Standard-Reaktionsenthalpie der homogenen Reaktion und zur Aktivierungsüberspannung in der Elektrodenreaktion.

Messungen der Temperaturabhängigkeit von Reaktionsgeschwindigkeiten in verdünnten Lösungen liefern Informationen über adiabatische und über dielektrische Sättigungseffekte. Absolute Reaktionsgeschwindigkeiten, zusammen mit der Kenntnis der Bindungskräfte und der Unterschiede in den Bindungslängen, erlauben zwar einen Einblick in das Gesamtbild, (systemgebunden adiabatisch, keine Sättigung Faktoren usw.).

Der gegenwärtige Stand der experimentellen Information über diese theoretischen Themen wird beschrieben.

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INTRODUCTION, ASSUMPTIONS, AND THEORY

WE SHALL review some of our results on the theory of electron-transfer reactions in solution and at electrodes,[1,2] which we have compared[2] with other treatments,[3,4] and then consider ways of testing experimentally various aspects of the theory.

The electron-transfer process in solution or at electrodes is considered in terms of a potential energy surface for the entire system. That surface is plotted as a function

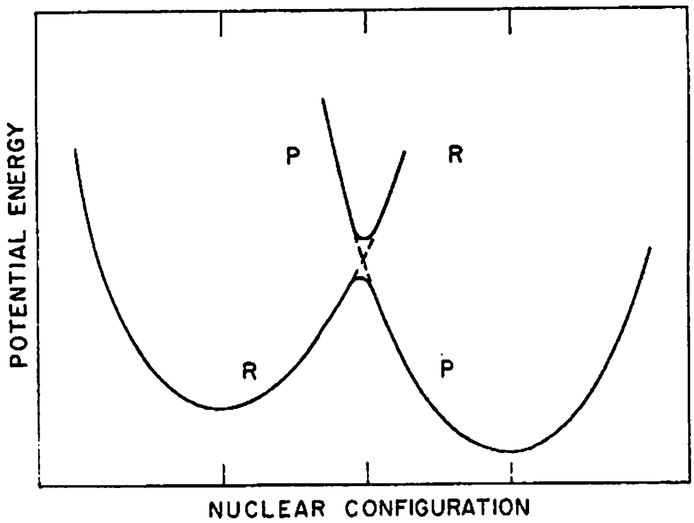

FIG. 1. Profile of potential energy surface of reactants (R) and that of products (P), plotted versus nuclear configuration of all the atoms in the system. ---, surface for zero electronic interaction of the reacting species. —, adiabatic surface.

of all co-ordinates of the system. These co-ordinates include bond lengths of the reactants, orientational co-ordinates of the solvent molecules, bond lengths and intermolecular distances of the latter, distance between the two reacting species and between each of them and the other molecules *etc.* The two "reactants" can either be two species in solution or one species and an electrode. Similar remarks apply to the "products".

A potential energy surface is first drawn for a system containing the two reactants and the rest of the system, without including the electronic coupling of the reactants (Fig. 1). A surface is also drawn for the two products, again without including coupling (Fig. 1). The two surfaces intersect at certain values of the co-ordinates. If there are N co-ordinates initially, this intersection set forms an $N - 1$ dimensional sub-space, which must be crossed for reaction to occur. When the electronic coupling is present the above surfaces are split at their intersection in a well-known quantum mechanical manner (Fig. 1, solid curves), yielding thereby a surface for a quantum mechanically adiabatic reaction.

When the system undergoes a suitable fluctuation of co-ordinates from values appropriate to reactants to values appropriate to the intersection region, it reaches the latter region and, one sees from Fig. 1, the electron transfer occurs if the coupling is strong enough. With strong enough coupling, the system continues to reside on the lowest surface, which is R initially and P finally. If the coupling is not strong enough, the system jumps from the lower R surface to the upper R surface, simply by retaining its original electronic configuration. The chance that the system remains on the lowest adiabatic surface on passing through the intersection region, and so yield a successful electron transfer, is then small. The reaction in this case can be said to have non-adiabatic aspects. The coupling is enhanced by decreasing separation distance between the two reactants. Thus, for electron transfer one needs a suitable fluctuation of co-ordinates and an appropriately small separation distance of reactants.

When an electrode reaction is involved, there are many R and P potential energy surfaces to be considered, each corresponding to different distribution of the electrons among the quantum states of the electrode. However, because of the Fermi distribution, most of the electron transfers occur to and from levels within kT of the Fermi level of the metal. For diagrammatic purposes in Fig. 1, therefore, the transfer can be visualized in terms of a simple averaged level.[1]

The details of the calculation of the electron-transfer rate have been given both for solution reactions and electrode reactions.[1] Part of the calculation involves obtaining an expression for the probability density of finding the system in the intersection region (per unit length along the abscissa of Fig. 1 in many-dimensional configuration space). Part involves use of a suitable expression for calculating the tendency of the system to remain on the lowest surface, and part involves the introduction of suitable approximations that simplify the theoretical expressions and permit their comparison with the experimental data.

The motion along the abscissa of Fig. 1 (in many-dimensional configuration space) has been treated classically.[3] (Thus, any "nuclear" tunneling through this barrier is ignored. It is normally regarded as minor except at low enough temperatures.) The reactions treated were those which did not involve rupture of a bond in the elementary step. For simplicity, the potential energy for stretching of bonds in the co-ordination shell of each reactant was treated as a quadratic function of the co-ordinates. In the statistical-mechanical calculation of the free energy of the ion–solvent and solvent–solvent interactions throughout the reaction a dielectric unsaturation (or at most partial saturation) treatment was used. Each reacting species was taken to have its co-ordination ligands intact, so that bridged activated complexes were not considered. A quasi-equilibrium distribution was used for computing the probability finding the system in the intersection region.

THEORETICAL EQUATIONS

For an electrode reaction (1) or a homogeneous reaction (2) the expression given by (3) was obtained for the rate constant,

$$\mathrm{Ox} + ne \rightarrow \mathrm{Red}, \tag{1}$$

$$\mathrm{Ox}_1 + \mathrm{Red}_2 \rightarrow \mathrm{Red}_1 + \mathrm{Ox}_2, \tag{2}$$

$$k = Z\kappa\rho \exp(-\Delta F^*/RT), \tag{3}$$

where ΔF^* is given by (4) for an electrode reaction and by (5) for a solution one,

$$\Delta F^* = \frac{w^r + w^p}{2} + \frac{\lambda_{el}}{4} + \frac{nF(E - E_0')}{2} + \frac{[nF(E - E_0') + w^p - w^r]^2}{4\lambda_{el}}, \tag{4}$$

$$\Delta F^* = \frac{w^r + w^p}{2} + \frac{\lambda}{4} + \frac{\Delta F^{\circ\prime}}{2} + \frac{(\Delta F^{\circ\prime} + w^p - w^r)^2}{4\lambda}. \tag{5}$$

Here, w^r is the work required to bring the reactants together until their separation distance R is R_0, the average R for those systems which react (*ie*, R_0 is the separation distance in the activated complex); w^p is the corresponding work term for the products for the same separation distance R_0 (R_0 is usually taken to be the distance of closest approach, but could be greater than that when the repulsions of reactants or products are large); λ and λ_{el} are intrinsic "reorganization factors", describing in energy terms the reorganization of co-ordinates needed when $E = E_0'$ or when $\Delta F^{o\prime} = 0$, expressions for them have been given;[1,2] n is the number of electrons transferred in the elementary step; E_0' is the "standard" potential of the half-cell for the prevailing temperature, medium, electrolyte, *etc*; E is the potential of the half-cell; $\Delta F^{o\prime}$ is the "standard" free energy of reaction under the prevailing conditions; Z is the collision number, and equals *ca* 10^{11} l/mol/s for a solution reaction and *ca* 10^4 cm/s for an electrode reaction; κ is an averaged probability of remaining on the lowest surface on passage through the intersection region ($\kappa = 1$ for an adiabatic reaction); ρ is a ratio of mean displacements (mean fluctuation in R_0 to mean fluctuation in "activated complex region" along the abscissa in Fig. 1),† being usually taken to be about unity.

Sometimes reactions (1) and (2) are preceded or followed by other elementary steps, but all properties in equations (3) to (5) refer explicitly to step (1) or step (2) itself.

COMPARISONS OF RATE CONSTANTS

We have summarized the deductions arising from (3) to (5).[1,2] (i) The rate constant of a homogeneous "cross-reaction", k_{12}, is related to those of the two electron-exchange reactions, k_{11} and k_{22}, and to the equilibrium constant K_{12}, in the prevailing medium by (6), when the work terms are small or cancel,

$$\mathrm{Ox}_1 + \mathrm{Red}_2 \overset{k_{12}}{\rightleftharpoons} \mathrm{Red}_1 + \mathrm{Ox}_2, \tag{2}$$

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}, \tag{6}$$

where

$$f = \frac{(\ln K_{12})^2}{4 \ln (k_{11}k_{22}/Z^2)}. \tag{7}$$

Frequently, f is within an order of magnitude of unity.

(ii) The electrochemical transfer coefficient at metal electrodes is 0·5 for small activation overpotentials (*ie*, if $|nF(E - E_0')| < |\Delta F_0{}^*|$, where $\Delta F_0{}^*$ is the value of ΔF^* for the exchange current), when the work terms are negligible.‡

(iii) When a substituent in the co-ordination shell of a reactant is remote from the central metal atom and is varied in a series, a plot of the free energy of activation ΔF^* versus the "standard" free energy of reaction in the prevailing medium $\Delta F^{o\prime}$ will have a slope of 0·5, if $\Delta F^{o\prime}$ is not too large (*ie*, if $|\Delta F^{o\prime}|$ is less than the intercept in this plot at $\Delta F^{o\prime} = 0$). In this series, for a sufficiently remote substituent, λ and the work terms are constant but $\Delta F^{o\prime}$ varies. The slope of the ΔF^* versus $\Delta F^{o\prime}$ plot has been termed the chemical transfer coefficient,[1] by analogy with the electrochemical terminology.‡

(iv) When a series of reactants is oxidized (reduced) by two different reagents, the ratio of the two rate constants is the same for all members of the series in the region of chemical transfer coefficients equal to 0·5 [*ie*, in the region where $|\Delta F^{o\prime}| < |\Delta F^*|_{\Delta F^{o\prime}=0}$ in each case].

† We have given[1] a more precise definition of ρ.
‡ See equation (87) of ref. 1 for a more general expression for this transfer coefficient.

(v) When the series of reactants in (1) is oxidized (reduced) electrochemically at a given metal/solution pd the ratio of the electrochemical rate constant to the chemical rate constant in (2) is the same for all members Ox of the series, in the region where the chemical and (work-corrected) electrochemical transfer coefficient is 0·5.

(vi) The rate constant of a (chemical) electron-exchange reaction, k_{ex}, is related to the electrochemical rate constant at zero activation overpotential, k_{el}, for this redox system, according to (8) when the work terms are negligible,

$$(k_{ex}/Z_{soln})^{1/2} \approx k_{el}/Z_{el}, \tag{8}$$

where Z_{soln} and Z_{el} are collision frequencies, namely about 10^{11} l/mol/s and 10^4 cm/s. (In (8) $\approx$ should be replaced by $\geqslant$ when the ion–electrode distance in k_{el} exceeds one-half the ion–ion distance in k_{ex}.)

TESTS OF THESE RELATIONS

Experimental tests of these various deductions have been summarized in recent surveys.[2,5] On the whole, the agreement is encouraging; there are four examples,[2,5] however (all but one involving cobalt complexes), where (6) is in error by factors of 10^3 to 10^6. Again, in the case of aromatic molecules or ions, electrode-reaction rates computed on the basis of homogeneous rates using (8) appear to be too fast.[6] Recently, the variation in electrochemical transfer coefficient α has been measured over a wide potential range, and found to be in reasonable agreement with (3) and (8).[7]

Comparisons of the experimental data of the type outlined in deductions (i) to (vi) test the similarity of various effects in the reactions being compared (*eg*, absence of spin restrictions, absence of highly specific effects), and test the effectively quadratic nature of the two surfaces in Fig. 1. (The vibrational potential energy was taken to be effectively a quadratic function of displacements in Fig. 1, and the ion–solvent free energy to be a quadratic function of functuations in local orientation polarization, according to the assumptions listed earlier.)

The principal discrepancy is expected to arise from highly specific effects (*eg*, influence of strong adsorption at an electrode), from non-adiabatic effects (*eg*, spin restrictions), or from different operative mechanism (*eg*, presence of excited electronic states in one reaction and not in another). In deduction (i) any breakdown of the quadratic behaviour of ΔF^*, particularly where $\Delta F^{\circ\prime}$ is large, could lead to serious numerical error.

ABSOLUTE VALUES OF A

Other deductions from equations (3) to (5) concern the numerical magnitudes of the quantities appearing in (3). Usually, experimental rate constants can be expressed as a function of temperature by

$$k = Ae^{-E_a/RT}, \tag{9}$$

where E_a, the activation energy, has an experimental definition

$$E_a = \frac{-R\partial \ln k}{\partial(1/T)}. \tag{10}$$

The experimental value of A can be a rather revealing quantity, both for electrode and solution reactions: If $\kappa\rho$ were about unity and if ΔF^* had no temperature dependence, A would equal Z. Thus, deviations of A from a value of *ca* 10^{11} l/mol/s (solution reactions) or 10^4 cm/s (electrode reactions) reflect either a temperature dependence of ΔF^* or a large difference in $\kappa\rho$ from unity.

If $-\partial\Delta F^*/\partial T$ is denoted by ΔS^* and if the minor temperature dependence of $Z\kappa\rho$ is ignored,

$$A = Z\kappa\rho \exp(\Delta S^*/R). \tag{11}$$

Non-adiabaticity can make κ much less than unity, and so tend to make A/Z small. ρ probably never deviates much from unity, though there are some special circumstances† where it could be as large as 10.

When coulombic repulsions or attractions become important, w^r and w^p can become quite temperature-dependent in a way well-known when the solvent can be treated as a dielectric continuum. The resulting value of ΔS^* can be quite different from zero, and that of A/Z quite different from unity. Addition of sufficient added electrolyte tends to make w^r and w^p small if the electrolyte introduces no other effects such as bridging. Then, the coulombic contribution to ΔS^* is also small. In homogeneous reactions which are not of the electron exchange type, $\Delta F^{\circ\prime}$ and $\Delta S^{\circ\prime}$ do not vanish. This $\Delta S^{\circ\prime}$ provides another contribution to ΔS^* which can also be quite large. Both contributions, coulombic and $\Delta S^{\circ\prime}$, are included in (4). In electrode reactions, $E - E^{\circ\prime}$ is usually held fixed as the temperature is varied, and so ΔS^* arises mainly from the $\mathrm{d}w^r/\mathrm{d}T$ and $\mathrm{d}w^p/\mathrm{d}T$ terms.

In the case of electrode reactions studied at high electrolyte concentrations, the experimental A/Z is typically unity,[8] to within a factor of 10, suggesting that $\kappa\rho$ is also. Few detailed studies of A are available for homogeneous reactions at high electrolyte concentration. For those studied at low concentration, $\mathrm{d}w^r/\mathrm{d}T$ and $\mathrm{d}w^p/\mathrm{d}T$ effects are very apparent. Typically, electron-exchange reactions between ions of like sign cause a large ordering of solvent molecules near the activated complex, because of the large charge on it, and cause $\Delta S^*/R$ to be quite negative, about -10 to -15 in some cases. This order of magnitude is the same as that calculated from differentiation of (4) with respect to temperature and using a dielectric continuum expression for the w's.

ABSOLUTE VALUE OF E_a

Since E_a is defined only by (10), a theoretical value of E_a can be obtained only by inserting the theoretical expression for $k(T)$ into (10), a fact overlooked in a a recent work[3] on $Fe^{2+} - Fe^{3+}$ exchange. For this reason, any temperature-dependent theoretical quantities such as w^r, w^p and $\Delta F^{\circ\prime}$ contribute to E_a not only in their own right but also through their temperature derivatives. Therefore, E_a does "not" equal ΔF^* exactly.

The numerical value of E_a is obtained by inserting (4) or (5) into (10) There are several contributions to E_a. In a reaction in which $\Delta F^{\circ\prime}$ vanishes (*eg*, in an electron-exchange reaction) or in an electrode reaction in which $E - E^{\circ\prime}$ vanishes, the intrinsic reorganization terms λ and λ_{el} are the principal contributors to E_a. These λ's contain a contribution fron the co-ordination shell of each reactant and a contribution from reactant–medium interactions: λ increases with increasing difference in "equilibrium" bond lengths or angles in each co-ordination shell before and after

† If the coulombic repulsion is so large, and the dependence of the dielectric contribution to λ on R_0 so small, that $\kappa \exp(-\Delta F^*/RT)$ varies but slowly with R_0, the ΔR_0 appearing in the theoretical expression for ρ might be appreciable.

reaction and with increasing difference in "equilibrium" polarization of the solvent at each point of the medium before and after reaction. λ depends, too, on the bond force constants. These effects are illustrated in Fig. 1.†

Since $\lambda/4$ is approximately the barrier height in Fig. 1, the theoretical expression for the solvent polarization contribution to λ bears one further comment. The dielectric continuum form[1] of this expression is easy to use but is necessarily approximate. The statistical-mechanical form[1] of this expression is simple in its appearance but requires for its evaluation a good, simple statistical-mechanical theory of equilibrium solvent–ion interactions.

Some information is available on force constants and bond lengths in co-ordination compounds. The various numerical calculations which have been made[3,4] are not too far from the observed E_a's, but the exact values of the pertinent force constants and bond lengths are often somewhat uncertain as yet. These changes in equilibrium bond lengths (and, in part, solvent polarization) are believed to account for the major observed differences in rates of electron-exchange reactions. Until recently, the extreme slowness of the homogeneous $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ exchange reaction was attributed to this source. However, recent crystallographic measurements[9] have revealed that the changes in equilibrium bond lengths were similar to those of a number of other (2+, 3+) co-ordination compounds which undergo an electron-exchange reaction at a much higher rate. The slowness of the $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ reaction may thus be due to a small value of κ.

Another reaction that is relatively slow is the $Co(phen)_3^{2+}$–$Co(phen)_3^{3+}$ exchange,[10] the reaction being much slower than the $Fe(phen)_3^{2+}$–$Fe(phen)_3^{3+}$ exchange. It is not yet known whether the slowness is due to a change in bond length effect or to a small value of κ. The former would cause E_a to be larger in the cobalt reaction while the latter would cause κ to be smaller in that reaction. Coulombic effects would be expected to cancel when ratios of the two rate constants are compared in this manner. Thus far, however, the $Fe(phen)_3^{2+}$–$Fe(phen)_3^{3+}$ has been too fast for study, and it may be necessary to resort to indirect studies, utilizing (6), to explore these effects.

ELECTRODE MATERIAL

We have not commented thus far on the nature of the electrode material.[11] It affects the rate in several ways: because of its surface charge and because of its adsorption, it influences the double layer and other contribution to w^r and w^p. When the difference $E - E_0'$ can be specified and controlled, differences in inner potentials in metal electrodes are automatically compensated by studying the reaction at a given $E - E_0'$. However, in other cases (some semiconductors, for example), $E - E_0'$ is unknown and has to be replaced by the theoretical expression from which it arose, an expression involving differences of electrochemical potentials at the

† The above contributions to λ are illustrated in Fig. 1 when $\Delta F^{\circ\prime}$ is zero: When the equilibrium bond length undergoes a large change as a result of reaction, the two curves in Fig. 1 are considerably displaced from each other horizontally. They then intersect only at a high potential energy and so yield a high E_a. The larger the force constants, the higher the potential energy at the intersection (Fig. 1) and the higher the E_a. Similarly, large changes in local equilibrium solvent polarization cause the two curves in Fig. 1 to be appreciably displaced from each other horizontally and increase E_a thereby. This polarization effect is large when the ion size is small and when the orientation polarization is large (*ie*, when the static and optical dielectric constants are quite different). All of these effects are evident from the equations available for λ and λ_{el}.

Increasing or decreasing the $\Delta F^{\circ\prime}$ at fixed λ corresponds to raising or lowering the P surface relative to the R one.

electrode/solution interface. In that case the nature of the electrode material appears explicitly.

OTHER APPLICATIONS AND CONCLUDING REMARKS

There are a number of other applications that can be made of (3)–(5) to various types of electron-transfer problems. For example, electron-transfer reactions of excited states are expected to obey (3) when the appropriate $\Delta F^{o\prime}$ and λ are introduced. The equations were used to formulate a theory of chemiluminescent reactions.[12] Again, the concepts were used to formulate a theory of solvated electron reactions, by allowing for the sensitivity of the charge cloud of the electron to solvent fluctuations.[13] We have considered some other applications elsewhere in the Elmau symposium. They include

1. thermal and photochemical electron transfer,[14]
2. the question of how much a standard free energy or energy deficit a reaction can tolerate and still occur,[15]
3. effect of vibrational readjustments on computed activation energies and on ratio of exchange currents at metals and degenerate semiconductors,[15]
4. atom-transfer reactions and possible modifications of the equations.[16]

Although much is understood about the nature of electron-transfer processes, there are gaps in our knowledge. The uncertainties will be removed with increased knowledge of bond lengths and force constants, increased experimental knowledge of non-adiabatic effects, of specific interactions such as bridging and adsorption, and of solvent–ion–electrode interactions. Our main tools in obtaining this knowledge may prove to be comparative studies of rate constants, such as those listed earlier, measurements of the Arrhenius pre-exponential factors A under conditions where coulombic effects are either negligible or well-understood, crystallographic measurements of bond lengths and angles, and vibrational spectroscopic measurements of force constants. The study of photochemically induced electron-transfer reactions could also add to this knowledge (if free radicals are not formed), by providing direct information on the role of excited states.

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† Hush's calculations can also be treated as a means for calculating the force constants and equilibrium bond lengths. The latter can then be introduced into Eqs. (4) and (5).

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DISCUSSION

X. de Hemptinne.—I want to comment on the part of your paper on heterogeneous reactions. I refer to your paper (*J. chem. Phys.* **43**, 679 (1965)) in which you argue that electron transfer takes place only when the system is at the crossing point of the potential energy surfaces for reactants and products. Your argument is that if E is some energy level of the reactant, the number of systems which may react is proportional to $\exp(-E/kT)$ (or perhaps $\exp(E/2kT)$. The partial current corresponding to this energy level is

$$i(E) = \mathrm{n}(\varepsilon)\,.\,\mathrm{f}(\varepsilon)\exp(-E/kT),$$

where $\mathrm{n}(\varepsilon)$ is the electron degeneracy and $\mathrm{f}(\varepsilon)$ the Fermi distribution for those metallic electrons which are involved in the transition to the molecule in its energy level E.

The total current is then

$$i = \int_0^\infty i(E)\,\mathrm{d}E\,,$$

and it turns out that the biggest contribution arises for systems with energies equal to that of the intersection point ($E = E_\pm$).

I continue to think that the overwhelming majority of contributions to the total current come from the ground-state configuration of the reactant, or from states lying within kT of the ground state. Solvent reorganization is a process that comes after the electron transfer.

Consider the vibration of the system in phase space. Every vibrational energy level is represented by an ellipse,

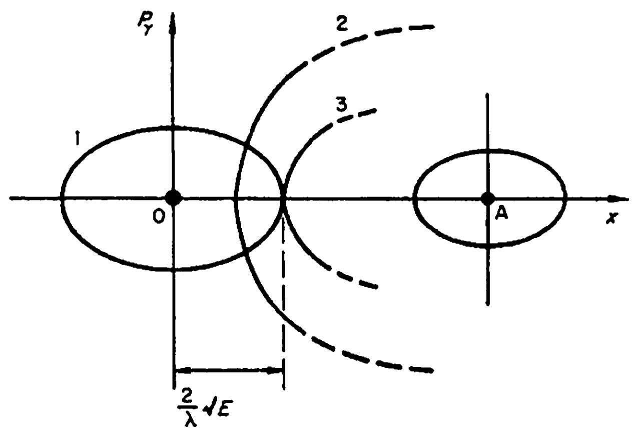
$$E = \frac{p_x^2}{2m} + \frac{\lambda}{2}x^2\,,$$

the major axis of which is

$$x_0 = \frac{2}{\lambda}\sqrt{E}\,.$$

The ground state is represented by the origin 0. The product of the reaction, R, must be treated in the same way and is represented in phase space by ellipses centred round R. The Franck-Condon

FIG. A.



principle states that the co-ordinates of the system in phase space are not changed during the electron transfer. This means that, starting from one point on an ellipse (say (1)) one gets after transfer a corresponding ellipse centred on R. Electron transfers starting from vibrational level (1) to give the product, and which requires the smallest amount of energy (which is supplied by the metallic electrons) are those which give rise to the tangent ellipse. Although it is possible to take account of all possible transitions, let us focus our attention on those for which $p = 0$, that is on those which go from one ellipse to the tangent one.

The total density of states with energy lying between E and $E + \mathrm{d}E$ is given by

$$N(E)\,\mathrm{d}E = \frac{N}{kT}\exp\left(-\frac{E}{kT}\right)\mathrm{d}E\,.$$

These states are homogeneously distributed around the ellipse. The number of states within dE from E and situated at the right place in phase space is therefore the total number, divided by the length of the ellipse and multiplied by dp,

$$N(E, p = 0)\,\mathrm{d}E\,\mathrm{d}p = \text{constant}\,\frac{\exp(-E/kT)}{\sqrt{E}}\,\mathrm{d}E\,\mathrm{d}p\,.$$

The transition probability is the product of this function with the corresponding electron density in the metal, and the total current is this transition probability, integrated over all possible $E(0 - \infty)$. Integration over dp may be done approximately by considering the p dependence of the transition probability as a δ function.

The most important contribution to the integral arises near $E = 0$ where actually the function $\exp(-E/kT)/\sqrt{E}$ is infinity, although its integral remains finite,

$$\int_0^\infty \exp\frac{(-E/kT)}{\sqrt{E}}\,\mathrm{d}E = \sqrt{\pi kT}$$

For values which are greater than kT, the function becomes rapidly negligible. It is not a real δ function, which is symmetrical and also much sharper, but it has the right property to prove my statement (*Bull. Soc. Chim. France* 2328 (1964)).

R. A. Marcus.—While there are many curves (2) or (3) for products which intersect curve (1) near 0 because of the large width of the conduction band, they normally lie far below the Fermi level. As a calculation based on the Fermi-Dirac distribution shows, such levels contribute negligibly to the rate;[1] most of the contribution comes from electrode energy levels within kT of the Fermi level. This fact is recognized by Levich and Dogonadze, Gerischer, and myself. The vacancy probability of a single quantum state of energy ε_1 in the metal is $\{\exp[(\varepsilon_F - \varepsilon_1)/kT] + 1\}^{-1}$. When ε_1 is far below the Fermi level ε_F, low enough to permit a product surface in my Fig. 1 to intersect a reactant one, one requires $\varepsilon_F - \varepsilon_1 \cong \lambda$. $\lambda/4$ is the barrier at zero overpotential. For a typical λ of about 25 Kcal/mol, this vacancy probability is about 10^{-18}.

The second half of your comment discusses the statistical mechanics incompletely: (1) there are many degrees of freedom other than one vibration, so that the calculation of states in $(E, E + \mathrm{d}E)$ has to be replaced by a more detailed phase space or quantum distribution; (2) the actual motion along the reaction co-ordinate leading from reactants to products has to be discussed. I give more detailed discussion of these two points elsewhere (*J. chem. Phys.* **43**, 679 (1965); Appendix III of *J. chem. Phys.* **46**, 966 (1966)).

H. W. Nürnberg.—I have just a brief comment on the aspect of the comparison of rate constants for homogeneous electron transfer and rate constants for electron transfer at electrodes. In one of your tables there was a very good agreement of the values for the system V(III)–V(II). We have carried out recently a number of experiments on this system in different supporting electrolytes containing ClO_4^-, Cl^- and other ions, using a new technique based on faradaic rectification, which allowed us to make measurements down to the μs range. Techniques of this time resolution are very sensitive even to not very pronounced adsorption of the depolarizer not detectable with more conventional methods.

Our results indicate that specific adsorption of the depolarizer at the mercury electrode is very probable. The adsorption of V(III) is likely to occur *via* ion pairs formed with the mentioned anions in the inner region of the double layer. This specific adsorption leads generally to an enhancement of the rate constant at the standard potential of the electrode process.

This change in rate constant often will be not of orders magnitude but well below a factor of say 10 or even 5. Thus usually the general trend will not be affected too severely. However, if very accurate comparisons are to be made one should bear in mind that specific adsorption of the depolarizer, which is quite common even for inorganic species, might be responsible for deviations, because adsorption is not allowed for in your theory at present. Thus I have some reservations on the surprisingly good agreement in systems such as V(III)–V(II) between the results obtained at the mercury electrode and for homogeneous electron transfer in solution.

R. A. Marcus.—On theoretical grounds, $k_{el}/10^4$ and $\sqrt{k_{ex}}/10^{11}$ are expected to agree exactly when (1) specific effects, such as the adsorption you mention, are absent, (2) work terms for both reactions are negligible, (3) the average ion–electrode distance in the activated complex equals one half that between the two homogeneous reactants, and (4) $\kappa\rho$ is unity for both reactions.

Thus, at the present time, an exact agreement is probably too much to expect, but an approximate one would be satisfactory. It is good to learn from your comment that the adsorption effect might well be below a factor of five. Data on the comparison of $k_{el}/10^4$ and $\sqrt{k_{ex}}/10^{11}$ and on the various factors above will be very helpful in enhancing our detailed knowledge of these processes.