
MODERN ASPECTS OF
ELECTROCHEMISTRY

*

No. 3

Edited by J. O'M. BOCKRIS and B. E. CONWAY

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PREFACE

THIS SERIES of monographs in Electrochemistry began at a time (1954) when the considerable increase in research activity in fundamental electrochemistry, characteristic of the present decade, had not yet been reflected in a general awakening of interest in this field among chemists. The publication of this third volume comes at a time when the part of publications in Physical Chemistry which are electrochemical in nature, has attained some 20 per cent of the whole. This follows a period in which research into the properties of ionic solutions had reached, more or less asymptotically, a limit in the 1940's and much inertia was associated with kinetic studies of the mechanism of electrode reactions.

The entry of electrode process chemistry, or 'Electrodics' as it is appropriately called, into a modern phase is evidenced in many directions. In its theoretical formulation, electrode kinetics is now treated with the formal thoroughness associated with consecutive *chemical* reaction kinetics in other fields, and its position of general significance in the physical chemistry of *heterogeneous* reactions is now well recognized. The old empirical field of corrosion engineering is now being replaced by an electrode kinetic understanding of the processes of metal dissolution, electrochemical metal oxidation and passivation. The role of potential in *electrochemical* reactions is recognized as analogous to the role of high pressure in the kinetics of homogeneous *chemical* reactions in condensed phases. A beginning is being made towards relating electrocatalysis to the properties of the material of the electrode regarded as a heterogeneous catalyst, and to the adsorption behaviour of intermediates and reactants at its surface, thus providing the fundamental basis for the rapidly developing technology of direct electrochemical energy conversion. The double layer is no longer regarded simply as an analogue of a parallel plate condenser, and hence adsorption and its relation to electrode kinetics begins to become more rationalized. Semiconductors are no longer only the province of Solid State Physics but are considered in conjunction with electrolytic solutions at their interfaces, thus forming the basis of the Electrochemistry of the Non-metals. Metal deposition no longer depends alone on the electroplater's art but is being rationalized by relation to electrode kinetics at the atomic level, to the properties of single crystal faces and to the mechanism of crystal growth from the vapour phase.

Organic chemistry, formerly dependent on solute molecules as relatively uncontrollable sources or sinks of electrons, now has available for this purpose electrodes under potentiostatic control, which makes possible a number of controlled syntheses on a more rational basis than by the older methods. The electrochemical basis of a number of important biological processes has been recognized, particularly with regard to the behaviour of natural polyelectrolytes in cells, the cell membrane and the neurone. Further, in the field of the initiation of gas discharge, the electrochemical basis of field ionization at the metal-'vacuum' (gas) interface has been recognized, which has many parallels with electrochemical ionization at the metal-solution interface.

The relation of these forward steps (perhaps one is justified in saying 'strides') in fundamental aspects of Electrochemistry to technology is not the subject matter of this series but of another, later, compilation. Without the realization, however, of the development of the technological tree from the fundamental seeds, little appreciation of the probable future of Electrochemical Technology can be made. Electrodictics, it may be submitted, is now somewhat in the position of Electronics in the 1920's. Metallurgy, seawater extraction, the stability of materials, synthetic chemistry, electrochemical machining and the electrochemical conversion of energy are all areas in which Electrochemistry is now seen to form the basis of the evolution of practical processes.

The great shift in emphasis in Electrochemistry towards the discipline of electrodictics does not, however, seem to give cause for change in the nature of the contents of this series. Thus, in understanding the fundamental aspects of electrodictic processes, it is first necessary to have a detailed understanding of the behaviour of the ionic reactants in the solution which forms one side of the electrode double layer. Hence, a chapter on the fundamental factors determining the kinetics of homogeneous ionic redox reactions in solution is presented; the considerations given will have obvious relevance to the more complex problems of redox reactions at the metal-solution interface. The reactant involved in the electrochemical hydrogen evolution reaction from acid media is the hydrated proton, and the chapter on 'Proton Solvation and Proton Transfer Processes in Solution' treats in detail the problem of the identity of the proton in solution and the electrochemical kinetics of its homogeneous transfer reactions. The contribution on electrochemical adsorption brings a comprehensiveness not previously given to a review of the subject and will provide western readers with some insight into the extent and originality of the Russian work in this field. In the Chapter on the mechanism of the

PREFACE

deposition of metals, a degree of kinetic analysis hitherto unusual in the subject has been included. Finally, the Chapter on the adsorption of intermediates in electrocatalysis reviews the methods now available for studies of adsorption of radical intermediates in consecutive electrode reactions and treats the subject in a quantitative kinetic manner which can provide a basis for interpretation of the behaviour of more complex intermediates involved in organic oxidations.

Philadelphia and Ottawa,
1964

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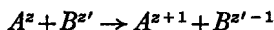
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THEORIES OF ELEMENTARY HOMOGENEOUS ELECTRON-TRANSFER REACTIONS

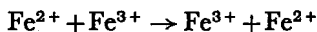
EDWARD SACHER and KEITH J. LAIDLER

I. INTRODUCTION

DURING recent years there has been considerable interest in the mechanism of reactions of the general type



in which there is an electron transfer from one ion to the other. An example of such a reaction is



Reactions of this kind may proceed by a direct electron transfer or may involve a more complicated mechanism; they may involve e.g. the transfer of an electron from one ion to a solvent molecule, with a subsequent transfer to the second ion. Sometimes an ion of opposite sign acts as a mediator in allowing the ions to approach one another.

The present review* is concerned with the theoretical aspects of reactions in aqueous solution in which there is a transfer of an electron from one ion to another and which occur in a single step. For simplicity, the discussion will deal largely with electron transfers between ions of the same type; in such reactions the products are the same as the reactants, and the rates are usually measured using isotopes. The theory of such symmetrical reactions is somewhat simpler and more straightforward than that of electron-transfer reactions between ions of different substances, but the general principles are the same.

The study of the mechanism of elementary homogeneous electron-transfer reactions provides an essential basis for consideration of the

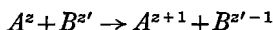
* Several other recent reviews have dealt with various aspects of electron-transfer processes; in particular may be mentioned the articles of DAINTON¹, HALPERN² and SUTIN³.

necessarily more complex heterogeneous electron-transfer reactions that occur in electrochemical redox processes and in metal deposition and dissolution.

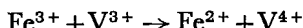
The general plan of the present review is as follows. The experimental results will first be outlined very briefly. An account will then be given of the main theoretical problems that must be dealt with in connection with these reactions. A description of the more important theoretical treatments of electron-transfer processes follows, with special reference to the assumptions and approximations involved and with a critical evaluation of each theory. Finally, an attempt will be made to give, on the basis of the previous theories, a more satisfactory theoretical treatment of non-adiabatic reactions of this type.

II. SURVEY OF EXPERIMENTAL RESULTS

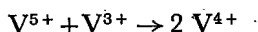
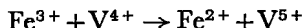
Reactions of the type



are frequently more complex than they appear to be and do not always involve a simple electron transfer. For example, the reaction

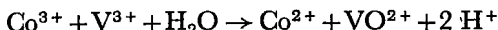


has been shown⁴ to occur not only by a direct electron transfer but, simultaneously, by the indirect transfer



The reaction by this mechanism is autocatalytic.

Another complication that may arise is found in the reaction



in which hydrolysis occurs⁴.

Mechanisms of these types are far from uncommon, and it is best for theoretical treatments to be confined in the first instance to reactions where there is direct transfer of a single electron. The present review is not concerned with mechanisms in which there is transfer through a bridge or in which a ligand is transferred together with the electron.

Electron-transfer reactions in aqueous solution can occur between total or partial aquo-ions; in the latter, ligands other than water are involved. This discussion will be limited to total aquo-ions.

Table 1 gives data for a number of electron-transfer processes which it is reasonable to regard as elementary. The fact that the kinetic parameters show no simple trends indicates that the reactions are

Table 1
Summary of Experimental Results for Electron-Transfer Processes in Ordinary Water

System	T °C	k l.mole ⁻¹ sec ⁻¹	E _a	ΔG [‡] kcal mole ⁻¹	ΔH [‡]	ΔS [‡] e.u.	Ref.
Cu ⁺ -Cu ²⁺ **	25	0.5 × 10 ⁸	—	6.99	—	—	5
Fe ²⁺ -Fe ³⁺	25	0.87	9.9	16.8	9.4	-25	6, 7
Cr ²⁺ -Cr ³⁺	24.5	< 1 × 10 ⁻⁵	22 ± 2	> 24.3	—	—	8
V ²⁺ -V ³⁺	25	1.0 × 10 ⁻²	13.2	20.1	12.6	-25	9
Co ²⁺ -Co ³⁺	0	~0.77	—	~16	—	—	10
Eu ²⁺ -Eu ³⁺	25	3.6 × 10 ⁻⁴	20.8	21.0	20.2	-3	11
Fe ²⁺ -Co ³⁺	0	10 ± 2	9.1	14.9	8.6	-23	12
Pu ³⁺ -Pu ⁴⁺	25	22	7.7	16	7.1	-31	13
Ce ³⁺ -Ce ⁴⁺	25	1.1 × 10 ⁻⁴	7.7	19	7.1	-40	14

* This reaction may be catalysed by Cl⁻ ions under the conditions used.

controlled by several important factors. Attempts to correlate the kinetic parameters with the nature of the complexes have met with very limited success^{4, 15}.

III. SOME THEORETICAL ASPECTS

A number of important theoretical problems arise in connection with the mechanisms of these electron-transfer reactions. In the present Section, in order to provide an introduction to the complete theories, some of these points will be considered briefly. All of them will be discussed in more detail in later Sections. It must be emphasized that there is still uncertainty with regard to some of the fundamental points.

The questions that will here be touched upon, and the answers arrived at, are:

(i) *Do the electron-transfer processes proceed by adiabatic or non-adiabatic mechanisms?* This is still uncertain; satisfactory theoretical treatments have been given from both points of view.

(ii) *Must solvent reorganization occur prior to electron transfer?* This is a logical necessity for an adiabatic mechanism; for a non-adiabatic one, a mechanism involving prior reorganization is favoured on energetic grounds.

(iii) Does the rate of diffusion of the ions towards one another affect the overall rate? It does so only for extremely rapid reactions and probably for none of those under consideration here.

(iv) In the treatment of electrostatic interactions, is it sufficiently satisfactory to treat the solvent as having a constant dielectric constant? In most cases a small but significant error is made if the effects of electrostriction are neglected.

1. Adiabatic and Non-Adiabatic Processes

Chemical reactions have frequently been classified as either 'adiabatic' or 'non-adiabatic', but unfortunately these terms have not always

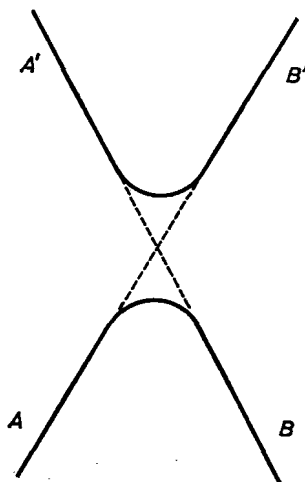


Figure 1. Schematic potential-energy curves for states of the same species—resonance splitting large

been used correctly. The fundamental principles involved are as follows. The course of any chemical reaction can be described as the movement of a mass point over a potential-energy surface, which is a surface (usually in many dimensions) obtained by plotting potential energy against the various coordinates that are required to give a complete description of the system. When such surfaces are constructed using the usual quantum-mechanical methods they are found to 'cross' one another at various places. Strictly speaking, when exact calculations are carried out there is never a real crossing, but there occurs a resonance splitting. Two extreme cases of what may occur at a crossing point are shown schematically in Figures 1 and 2,

SOME THEORETICAL ASPECTS

which represent sections through the surfaces. In *Figure 1*, the two surfaces correspond to states of the same species, which means that they have the same values of the quantum numbers Λ and S and the same symmetry properties. When this is the case, the probability of a crossing between the two surfaces is small; that is to say, a system initially on the lower surface, AB , has little chance of crossing to the upper surface $A'B'$, and vice versa. (The actual transition probabilities are considered in the Appendix.)

For states of different species, i.e. states that do not have the same symmetry properties and the same values of Λ and S , the resonance

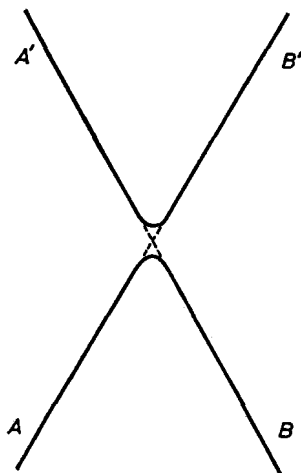


Figure 2. Schematic potential-energy surfaces for states of different species — resonance splitting small

splitting is small, as shown in *Figure 2*. The probability of transition between upper and lower surfaces is now close to unity, while that of staying on the upper or lower surface is close to zero. For example, a system at A and moving towards the 'crossing' point will tend to go towards B' rather than towards B . This is equivalent to saying that the system behaves as if the surfaces really crossed.

Another matter of importance is that, whether there is a large or a small resonance separation, i.e. whether *Figure 1* or *Figure 2* applies, there is a possibility of a transfer by quantum-mechanical tunnelling. This is illustrated schematically in *Figure 3*. A system that is at the state represented by the point P may pass to the state Q without

actually passing over the top of the barrier. The laws of quantum-mechanical tunnelling are discussed in the Appendix; here it is sufficient to note that tunnelling is favoured in the following circumstances:

- (i) when the process involves the transfer of a light particle (tunnelling is particularly important with electrons);
- (ii) when the particle is transferred only through a short distance;
- (iii) when the barrier is low.

The exact shape of the barrier is also of importance.

It may be seen that electron transfer from one ion to another may occur under three sets of circumstances:

(a) by passage of the electron over a barrier at the top of which there is a large resonance splitting (*Figure 1*): if the electron has sufficient energy to cross, the probability of crossing is unity;

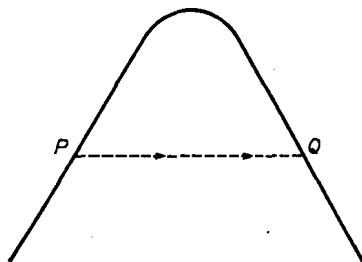


Figure 3. Tunnelling through a potential-energy barrier

(b) by passage over a barrier at the top of which there is a small resonance splitting (*Figure 2*): the probability of transfer is small, since the electron will tend to remain on the same surface;

(c) there may be quantum-mechanical tunnelling through a barrier of either type: the probability now depends on the nature of the barrier and is generally small.

The terms 'adiabatic' and 'non-adiabatic' have here been avoided, since their use may lead to confusion unless the situation is clearly understood. The use of the terms stems from the so-called 'adiabatic principle', first formulated in 1916 by EHRENFEST¹⁶. According to this principle, a system will remain in a given energy eigenstate when changes (e.g. in inter-atomic distances) are made at a vanishingly low rate. Thus, if the motions are very slow, a system starting at *A* in either *Figure 1* or *Figure 2* will end at *B* and not at *B'*; if the motions

are sufficiently fast, on the other hand, systems starting at *A* will end at *B'* rather than at *B*. The behaviour found with large and with small resonance splittings is thus qualitatively the same; the difference is that normal velocities result in a passage from *A* to *B* in the case of *Figure 1* and from *A* to *B'* with *Figure 2*.

Strictly speaking, the term 'adiabatic' should be reserved for the situation in which the transition is of the same character as that which occurs when the interatomic motions are vanishingly slow. Thus in the case of both *Figures 1* and *2*, transitions from *A* to *B* over the barrier should be described as adiabatic. Unfortunately the term 'non-adiabatic' is frequently applied to reactions of low transition probability, and the transition from *A* to *B* in *Figure 2* would be referred to as 'non-adiabatic' in this sense.

The case of *Figure 3*, in which there is quantum-mechanical tunneling, is correctly described as non-adiabatic, since the electron moves so fast that the nuclear motions cannot keep pace with it.

Fortunately the two cases of special interest in connection with electron-transfer reactions are those represented by *Figures 1* and *3*, and the terms 'adiabatic' and 'non-adiabatic' as applied to these cases present no ambiguity.

As will be seen, electron-transfer reactions have been treated from both points of view, and it is not yet possible to decide which mechanism applies.

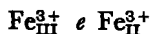
2. Solvent Reorganization

Reactions such as



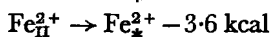
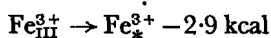
are symmetrical in the sense that reactants and products are identical. If such a reaction proceeds adiabatically it involves passage over a potential-energy barrier that corresponds to a symmetrical arrangement of the ions. This at once raises a problem as far as the solvent molecules are concerned. Ferric ions at equilibrium in aqueous solution are hydrated in a particular manner, and the symbol $\text{Fe}_{\text{III}}^{3+}$ will be used to denote a ferric ion having its normal hydration shell. Similarly, the symbol $\text{Fe}_{\text{II}}^{2+}$ will be used to denote a ferrous ion surrounded by its normal hydration shell. Suppose that $\text{Fe}_{\text{III}}^{3+}$ and $\text{Fe}_{\text{II}}^{2+}$ approach one another and that an adiabatic transfer of an electron occurred from the ferrous to the ferric ion, without any change in the solvent environment of each ion. The resultant products would be

$\text{Fe}_{\text{III}}^{2+}$ and $\text{Fe}_{\text{II}}^{3+}$, in which each ion is surrounded by a hydration shell of the 'wrong' type. The activated complex, in which the electron is on its way from the ferrous to the ferric ion, would be represented as

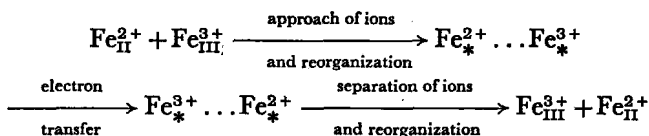


and is obviously unsymmetrical.

There are two ways by which this difficulty could be avoided. If the transfer of the electron could be regarded as occurring very slowly, the solvent atmospheres could reorganize themselves as the electron moved, and the activated complex would then involve a symmetrical arrangement of solvent molecules about the ion pair. This, however, is not realistic since the electron moves much more rapidly than the water molecules. The alternative is for the solvent shells to undergo partial reorganization *prior* to the electron transfer; the electron only moves after the stage has been set by the suitable movement of the water molecules. The water molecules in $\text{Fe}_{\text{III}}^{2+}$ are held somewhat closer to the ions than in $\text{Fe}_{\text{II}}^{2+}$, the distance (from the centre of the ion to that of the nearest water molecules) being 2.05 and 2.21 Å, respectively. The solvent reorganization will therefore involve a slight swelling of the hydration shell about the ferric ion, and a slight contraction of that about the ferrous ion; these movements must occur to an extent that causes the solvent atmosphere to become essentially the same about each ion. These solvent reorganization processes may be represented as



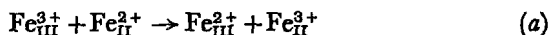
where the asterisk denotes intermediate hydration (the values are included in anticipation of the subsequent treatment). The overall process thus occurs as



Various attempts have been made to calculate energies of solvent reorganization, and the results are considered later; here it will be sufficient to indicate approximate values. For the conversion of $\text{Fe}_{\text{III}}^{3+}$ into $\text{Fe}_{\text{II}}^{3+}$ an energy of about 54 kcal mole⁻¹ is required, and about 30 kcal is needed for the conversion of $\text{Fe}_{\text{II}}^{2+}$ into $\text{Fe}_{\text{III}}^{2+}$. The energies required in an electron-transfer process are, however, very much smaller than these, since only a partial reorganization (i.e. from

$\text{Fe}_{\text{III}}^{3+}$ into Fe_{*}^{3+}) is required. The calculations, to be considered later, indicate that for the $\text{Fe}_{\text{III}}^{3+}$ and $\text{Fe}_{\text{II}}^{2+}$ ions the total energy of reorganization into $\text{Fe}_{*}^{3+} + \text{Fe}_{*}^{2+}$ is about $6.5 \text{ kcal mole}^{-1}$.

If the electron transfer is a non-adiabatic process, involving quantum-mechanical tunnelling through an energy barrier, there is no longer any *logical* necessity for solvent reorganization prior to electron transfer; in such a case the activated complex need not be symmetrical, and the reaction might follow different paths in the two directions (this would be a case of *hysteresis*). The true reason for solvent reorganization is that it allows the reaction to proceed by a path that is energetically much more favourable than is the case otherwise. Suppose that the electron transfer were to occur without prior solvent reorganization; then, since the transfer is much more rapid than the reorganization, the process would initially be



the products formed in this stage being the ions having hydration shells of the wrong type. The processes



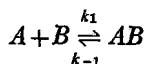
are endothermic by about 30 and 54 kcal mole^{-1} , respectively, so that reaction (a) is endothermic by 84 kcal mole^{-1} . The overall activation energy for the process is therefore at least this, and reaction by this mechanism would be exceedingly slow.

3. Rate of Diffusion

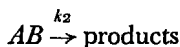
Before electron transfer can occur, the ions must diffuse together. The probability of transfer is greater the closer to one another are the ions, but since ions of the same sign must diffuse together against an electrostatic energy barrier they rarely approach one another very closely. The most favourable reaction path, therefore, involves a compromise between these two factors. A transition at short distances will be unlikely because of the repulsive energy, while one at large distances will be unlikely since the transfer itself will be of low probability; there will therefore be an optimum distance, which calculations indicate to be a few Å.

Since the ions must diffuse together, it might be thought that the actual rate of diffusion will enter into the overall rate expression; if this were so, the rate would depend on the diffusion constants of the ions and on the viscosity of the medium. For the actual reactions under consideration, however, the rates of diffusion are not likely to enter in an important way into the overall rate expression. That this

is the case may be seen on the basis of the following over-simplified model for the reaction. The approach and separation of the ions A and B may be represented as



where AB represents the two ions at the optimum separation, and k_1 and k_{-1} are the rate constants for the formation of these ion pairs and for the separation of the ions. The actual electron transfer may be represented as



where k_2 is the rate constant.

Application of the steady-state treatment gives

$$k_1[A][B] - (k_{-1} + k_2)[AB] = 0 \quad (1)$$

whence

$$[AB] = \frac{k_1}{k_{-1} + k_2} [A][B] \quad (2)$$

so that the rate of the overall reaction is

$$v = k_2 [AB] \frac{k_1 k_2}{k_{-1} + k_2} [A][B] \quad (3)$$

Two special cases may be considered. If the rate of the electron transfer is rapid enough that $k_2 \gg k_{-1}$, the rate becomes

$$v = k_1 [A][B] \quad (4)$$

The overall rate is then the rate with which the ions diffuse together, and the reaction is said to be *diffusion-controlled*. If, on the other hand, the electron transfer is so slow that $k_2 \ll k_{-1}$, the rate is

$$v = \frac{k_1}{k_{-1}} k_2 [A][B] \quad (5)$$

In this case, from equation 2,

$$[AB] = \frac{k_1}{k_{-1}} [A][B] \quad (6)$$

so that the AB pairs are at equilibrium with A and B . The rate is now not controlled by the rate of diffusion of the ions to one another but depends on the equilibrium between A , B and AB . This depends