The Theory of Thermal Electron-transfer Reactions in Solution

By I. Ruff
INSTITUTE OF INORGANIC AND ANALYTICAL CHEMISTRY, L. EÖTVÖ
UNIVERSITY, BUDAPEST

1 Introduction

Inorganic reactions in solution can be classified, in general, as belonging either to acid–base or to electron-transfer reactions. All reactions of mono- and poly-nuclear complex formation as well as those of precipitate formation, an extreme case of the latter, are included in the group of acid–base reactions, if the definition of acid and base is broad enough as, *e.g.*, Lewis's one.

Electron-transfer reactions take place between two or more chemical objects by electron donation and acceptance and these chemical objects are initially and finally moving independently of each other. Neutral molecules, ions, and compact materials (electrodes) may serve as chemical objects. The initial and final independence of the reactants excludes the electron-transfer processes within the same molecule, such as the case of charge-transfer complexes.

In most cases the electron-transfer reaction is accompanied by acid–base processes, since the change in oxidation number, which is the result of the reaction, influences the acid–base properties of the reactant particles [see, *e.g.*, the iron(II)–permanganate reaction]. It is generally assumed that, in the electronic excitation, changes in the co-ordination sphere such as protonation or deprotonation, *i.e.*, acid–base phenomena, precede the electronic jump. Electron transfer is, however, the principal process determining the total free-energy change predominantly through electronic energies.

Sometimes the electronic jump is believed to take place simultaneously with the transfer of a 'heavy' particle, such as proton (H atom transfer in organic oxidation), oxygen, or any other ions, atoms, or groups of atoms. As these reactions can be regarded to be simultaneous electron-transfer and acid–base reactions, it seems that there is no basic reason for distinguishing between electron and atom transfers in oxidation–reduction reactions as is done frequently.

The terms 'oxidation–reduction' and 'electron-transfer reactions' are usually applied as identical ones. For simplicity the expression 'oxidation–reduction' will be used in this Review for conventional electron transfers with *finite* change in reaction free energy, while 'electron exchange' will refer to those of zero net free energy change (isotopic exchanges between ions of the same element in different oxidation states). 'Electron transfer' will cover both.

Electron-transfer reactions play a very important rôle in almost every field of

chemistry, and in certain important phenomena of biology, such as photosynthesis, reactions in the respiratory chain of cells, etc. This explains the enormous volume of experiments and theoretical work that have been published. In this Review only the theoretical treatments for homogeneous electron-transfer reactions will be considered, with reference to heterogeneous electrode reactions only when the theory predicts relations for both. Experimental results will be quoted only in comparing them with theoretical predictions. 'Pure' electrochemical theories as well as those dealing with radiation- induced electron-transfer reactions will be omitted.

A number of reviews and books have dealt with this field.[1-9] Recent developments, however, call for an up-to-date comparison of the applicability of the different theories. Hence instead of the concrete treatment, the physical meaning of the models and the conclusions will be discussed first; theories starting from identical models but differing in mathematical apparatus, will not be treated individually.

Any theoretical approach for chemical reactions starts from assumptions on the microscopic processes, *i.e.*, on the model of the mechanism. Its correctness can then be confirmed by deducing relations for kinetic parameters that can be experimentally observed. Unfortunately the number of measurable quantities of these reactions is small; this is why the theories outlined by different authors are based on such different, contradicting principles. At the present stage there is not any *direct* proof of the correctness of one of the activated complexes supposed, so the applicability of a model can be judged from two viewpoints: (i) which model is more plausible and (ii) which can predict results in satisfactory agreement with experiments over a broader range of parameters and reactions.

2 The Franck–Condon Principle and Its Application for Radiationless Transitions
The Franck–Condon principle,[10] so important in interpreting molecular spectra, yields information on the probability of transitions among electronic levels due to different vibrational states. This schematic conception is that the transition of an electron from one level to the other cannot be accompanied by simultaneous nuclear displacement, since the mass of the electron is much smaller than that of the nuclei. If energy relations are schematically indicated in a diagram of energy as a function of internuclear distance, as in Figure 1, electron transfer could occur only between terms having vibrational eigenfunction with a

[1] R. R. Edwards, *Ann. Rev. Nuclear Sci.*, 1952, **1**, 301.
[2] C. B. Amphlett, *Quart. Rev.*, 1954, **8**, 219.
[3] B. J. Zwolinsky, R. J. Marcus, and H. Eyring, *Chem. Rev.*, 1955, **55**, 157.
[4] F. Basolo and R. G. Pearson, 'Oxidation–Reduction', in 'Mechanism of Inorganic Reactions', J. Wiley and Sons, New York, 1958.
[5] H. Taube, 'Mechanism of Redox Reactions', *Adv. Inorg. Chem. Radiochem.*, 1959.
[6] J. Halpern, *Quart. Rev.*, 1961, **15**, 228.
[7] H. Taube, *Proc. R. A. Welch Foundation Conf. Chem. Res.*, 1962, 7.
[8] R. A. Marcus, *Ann. Rev. Phys. Chem.*, 1964, **15**, 155.
[9] E. S. Amis, 'Solvent Effects on Reaction Rates and Mechanisms', Academic Press, New York and London, 1966.
[10] E. U. Condon, *Phys. Rev.*, 1940, **36**, 1121; E. U. Condon and G. H. Shortley, *ibid.*, 1931, **37**, 1025.
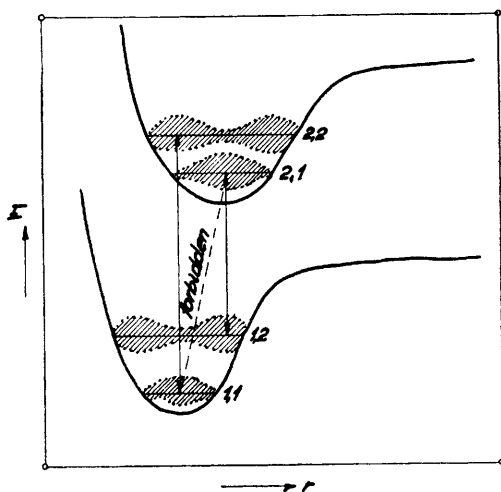
Figure 1 *Schematic representation of the electronic transitions regulated by the Franck–Condon principle*

maximum at the same *r*. (The density of the electron clouds is symbolised by hatching. For lower vibrational levels the maximum is somewhere in the middle of the potential well; for higher levels it is around the turning points, that is, at the wall of the potential well.) The ground state, corresponding to the new bond relation created by electron transition, can be occupied by the system only after the electron transition has taken place, after a relaxation period determined by the nuclear masses.

In Figure 1 electron transitions accompanied by bond relaxation are schematically represented. Electron transition can thus occur only vertically (*r* = constant), *i.e.*, only the 1,1 → 2,2 and 1,2 → 2,1 transitions are permitted.

Libby's fundamental idea was that these transition probabilities are valid for radiationless electron transitions, and so for electron transfer reactions as well.[11,12] In this case the 1,1 and 1,2 states belong to the reducing agent in the reaction, the 2,1 and 2,2 states belong to the oxidising particle. When the discussion is limited to electron-exchange reactions in which reactants and products are chemically identical, the standard enthalpy change of the reaction need not be considered, since the 1,1 and 2,1 levels are energetically identical. For instance, let the 1,1 level be the ground state of the aquated Fe^{2+}, and consider reaction (1).

$$Fe^{2+} + *Fe^{3+} \rightleftharpoons Fe^{3+} + *Fe^{2+} \tag{1}$$
$$\text{(1)} \qquad \text{(2)} \qquad \text{(1)} \qquad \text{(2)}$$

It is evident that in the final state of the reaction the electronic energy is identical with that of the initial state. With the same example, electron exchange can

[11] W. F. Libby, *J. Phys. Chem.*, 1952, **56**, 863.
[12] H. C. Hornig, G. L. Zimmermann, and W. F. Libby, *J. Amer. Chem. Soc.*, 1950, **72**, 3808.

occur as follows: (a) If the electron starts from the ground state of Fe^{2+}, it can be 'received' by Fe^{3+} only if the water molecules in the first co-ordination sphere are in an excited vibrational state corresponding to the 2,2 level. A part of the ativation energy thus has to be supported to excite the vibrational state of Fe^{3+} so that, on receiving the electron, the water molecules should be in an excited state corresponding to the Fe^{2+} ion. The reaction is then terminated by the 2,2 → 2,1 transition, *i.e.*, by accepting the electron the formerly tervalent iron ion has become an excited bivalent iron ion, then an Fe^{2+} ion in the ground state.

(b) The reaction path *via* 1,1 → 1,2 → 2,1 states is completely analogous to what has been shown above; moreover, it can easily be seen that its activation requirements are the same, since in an electron exchange reaction the intermediate and ground levels are identical.

Both in (a) and (b) a symmetrical arrangement of the neighbourhood with respect to the plane perpendicular to the Fe–Fe axis is produced so that the electron cannot 'distinguish between its original and new owner'. There are intermediate cases, of course, when this symmetry requirement is fulfilled by simultaneous changes in *both* co-ordination spheres.

These were essentially Libby's assumptions. His most important conclusion was that for ion pairs for which there is no or only very small difference in the first co-ordination sphere of the oxidised and reduced form, like $Fe(CN)_6^{4-}$– $Fe(CN)_6^{3-}$ and MnO_4^{2-}–MnO_4^{-}, the Franck–Condon restriction does not lead to any appreciable energy barrier and these reactions are expected to proceed quickly. At the time of Libby's report, these electron-exchange reactions were known to be unmeasurably fast.[13–15] Yet measurements on the Fe^{II}–Fe^{III},[16] Ce^{II}–Ce^{IV},[17] and Eu^{II}–Eu^{III} systems[18] yielded measurable and slower rates.This was in accordance with Libby's ideas, for the bond strength of water molecules is markedly different in these cases for ions of different charge. Numerical data cannot be derived by this theory, since quantum mechanical knowledge of the system is needed and this is almost inaccessible.

The reaction rate depends also on the distance between the two reacting particles. Therefore, in addition to the activation energy due to the Franck–Condon restriction, energy is required to bring the particles from an infinite distance to a distance necessary for reaction. This can be roughly approximated by the electrostatic repulsion, if the solvent is considered to be a continuous dielectric medium.

The value of the enthalpy of activation, $\Delta H^{\ddagger}$, is considerably reduced by a negative ion placed between the ions. For this reason Libby attributed catalytic effects to small negative ions. This accelerating effect is the greatest when the negative ion is built in in the first co-ordination sphere of the reactant ions,

[13] N. A. Bonner and H. A. Potratz: *J. Amer. Chem. Soc.*, 1951, **37**, 1845.
[14] R. C. Thompson, *J. Amer. Chem. Soc.*, 1948, **70**, 1045.
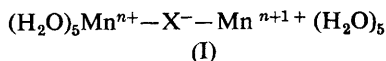[15] J. W. Cobble and A. W. Adamson, *J. Amer. Chem. Soc.*, 1950, **72**, 2276.
[16] J. Silverman and R. W. Dodson, Brookhaven Quart. Report, BNL-93, p. 65, 1950.
[17] J. W. Gryder and R. W. Dodson, *J. Amer. Chem. Soc.*, 1949, **71**, 1894.
[18] D. J. Meier and C. S. Garner, *J. Amer. Chem. Soc.*, 1951, **73**, 1894.

forming a bridge for electron transfer, as for example, in the activated complex (I), where X^- may be F^-, Cl^-, OH^-, etc.

$$(H_2O)_5 Mn^{n+} - X^- - Mn^{n+1+} (H_2O)_5$$
$$(I)$$

Though Libby's hypothesis is qualitative, it has been the starting point for most of the theories developed so far. They can be divided into two groups: (i) the so-called 'outer sphere' mechanism which deals with systems involving reactant ions of 'hard' co-ordination spheres, and (ii) the 'inner sphere' mechanism. In this case the reactant ions are suitable for formation of the binuclear activated complex (I). The latter group of reactions seems to be the more difficult for theoretical treatment, so we shall deal with it after the outer sphere transfers.

3 The Outer Sphere Mechanism
A. Theories in which Direct Transfer is Assumed.—(i) *Application of the tunnel effect.* The first theory yielding *quantitative* results comparable with the measurements was published by Eyring *et al.*[19] Libby's assumption for the outer sphere mechanism was entirely retained, but it was completed by an important aspect, namely the transfer probability of the electron which can easily be calculated on the basis of quantum mechanical tunnelling. According to this model, the main steps of the reaction are: (1) The collision of the reactant species which needs an energy equal to the Coulomb repulsion. (2) The Franck–Condon restriction requires the rearrangement of the environment owing to the new charge distribution, resulting from the transfer: the water molecules, being almost 'frozen' in the electrostatic field of the ions, are to 'melt' to make the rearrangement possible. (3) The electron must appear where the oxidising ion is located and this does not occur with unit probability.

The Franck-Condon principle as applied by Libby does not take into account that the electron must be transferred into a field of a nucleus chemically identical with the original, but different in its space co-ordinates. The electron thus is not only subjected to energy changes, but it must cover a definite route in space, which is not without obstacles. The potential barrier to be passed by the electron is, in this approach, the sum of the Coulomb potential of the reactants (see Figure 2). Since to a first approximation this potential barrier can be replaced by a triangular potential, the transfer probability, χ_e, is given by equation (2),

$$\chi_e = \exp\left(-\frac{\Delta F_{\ddagger}^{+} \text{ tun.}}{RT}\right) = \exp\left\{-\frac{8\pi}{3h} r_{n,m} \sqrt{\left[2m\left(V_0 - W\right)\right]}\right\} \quad (2)$$

where m is the mass of the electron, V_0 is the height of the potential barrier, and W is the kinetic energy of the electron. V_0 can be calculated with respect to the ionic charges and the interionic distance, $r_{n,m}$, while W can be obtained as the half of the potential energy of the electron, according to the virial theorem.

The total activation free energy is given by equation (3). The first and third

[19] R. J. Marcus, B. J. Zwolinsky, and H. Eyring, *J. Phys. Chem.*, 1954, **58**, 432.

$$\Delta F\ddagger = \Delta F\ddagger_{rep.} + \Delta F\ddagger_{rearr.} + \Delta F\ddagger_{tun.} \tag{3}$$

term of the right-hand side of equation (3) is determined by equation (2) and by a simple electrostatic interaction term, respectively.
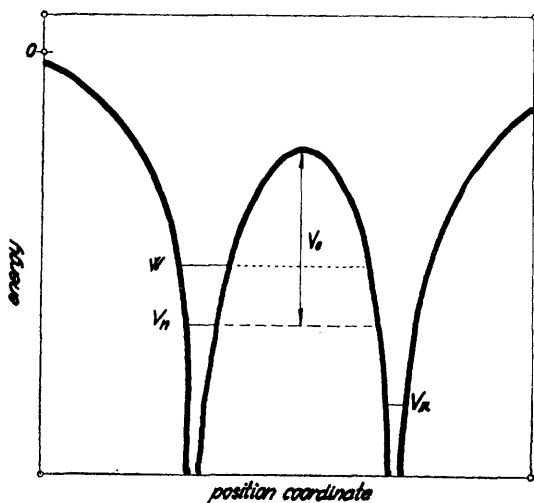

Figure 2 *Electrostatic potential barrier between two ions of positive charge* (Reproduced from *J. Phys. Chem.*, 1954, **58**, 432 by permission)

The *a priori* calculation of $\Delta F\ddagger_{rearr.}$ is very difficult, but this portion of the activation free energy was supposed to be approximately constant. Thus there should be parallelism between the total activation free energy calculated without $\Delta F\ddagger_{rearr.}$ and the measured ones. The reaction of Fe^{II} to Fe^{III} was chosen for fitting and the 8·1 kcal./mole difference obtained was considered for each reaction as $\Delta F\ddagger_{rearr.}$.

Since the repulsion term is enhanced by decreasing $r_{n,m}$, while the tunnelling term is reduced, there is an optimal interionic distance $r^*_{n,m}$ that can be calculated by minimising the total free energy of activation. The minimum appearing at $r^*_{n,m}$ represents the value which is due to the fastest path, *i.e.*, the observed one.

The calculated and experimental values are compared in Table 1. Agreement between the values is not always satisfactory. The $r^*_{n,m}$ values show that apart from the reacting ions and the ligands in their first co-ordination sphere no other ..icle is implied in the activated complex, as they generally approach one another up to the contact of these spheres. Thus the error in assumptions arising from treating the solvent as a dielectric medium is immediately revealed.

Apart from its semi-empirical nature, this theory has other essential deficiencies. On one hand, it cannot interpret the electron exchange between negatively charged ions as, *e.g.*, $MnO_4^{2-}-MnO_4^{-}$; in this case there would be three potential wells for the electron; two in the vicinity of Mn^{VII} and Mn^{VI} and one *between* the two negative ions which is obviously meaningless. On the other hand, it is

Table 1

Reaction	$r^*_{n,m}$ (Å)	$\Delta F_{\ddagger}^{\ddagger}$ (kcal./mole)	
		Calc.	Obs.
$Co(en)_3^{2+}$–$Co(en)_3^{3+}$	5·9	16·8	23·5[b]
Tl^+–$Tl(OH)^{2+}$	3·3	13·3	23·9[c]
$V(OH)^{2+}$–VO^{2+}	4·4	16·0	17·2[d]
Fe^{2+}–Fe^{3+}	5·0	16·7[a]	16·7[e]
Fe^{2+}–$Fe(OH)^{2+}$	4·9	15·1	12·2[e]
Fe^{2+}–$FeCl^{2+}$	4·9	15·1	15·3[e]
Fe^{2+}–$FeCl_2^+$	3·4	13·1	15·1[e]
Ce^{3+}–Ce^{4+}	9·3	19·1	18·0[f]

[a] Fitted value. [b] W. B. Lewis, C. D. Coryell, and J. W. Irvine, *J. Chem. Soc., Suppl. No. 2*, 1949, s386. [c] G. Harbottle and R. W. Dodson, *J. Amer. Chem. Soc.*, 1951, 73, 2442. [d] S. C. Furman and C. S. Garner, *J. Amer. Chem. Soc.*, 1952, 74, 2333. [e] See Ref. 32. [f] J. W. Gryder and R. W. Dodson, *J. Amer. Chem. Soc.*, 1951, 73, 2890.

not clear why it is the kinetic energy of the electron of the ground state that is considered, when the transfer state is vibrationally excited because of the free energy of rearrangement which it possesses.

Marcus criticised[8] the electron-tunnelling hypothesis because of the omission of the probability factor p that expresses the number of times the electron 'strikes' the barrier wall (about 10^{16} sec.$^{-1}$). The right probability should be $p\chi_e$ instead of χ_e. However, in view of the method of deduction of equation (2),[20] and the invariability of χ_e with respect to the amplitude of the 'striking' electronic wave, Marcus's criticism can be rejected. For, if an electron is in its initial state, it will be on the other side of the barrier with probability χ_e, independently of whether it strikes the wall p times forwards and $p\chi_e$ times backwards, since the chance of finding an electron in its initial state is always χ_e times greater than that of finding it in the final state.

It must be mentioned that Randles[21] published independently a theoretical treatment for electrode reactions on an almost identical basis to Eyring's one. Weiss's model,[22] however, which appeared in the same year does not take the rearrangement *before* the electron transfer into account.

By refinement of the model Laidler[23] eliminated some of the inadequacies, but he could not solve the main contradictions. Two essential changes have been affected in the premises: (i) In place of dielectric constant, the refractive index, which is more relevant to short distances, has been considered. (ii) In place of the Franck–Condon restrictions the activation free energy ($\Delta F_{\ddagger}^{\ddagger}$diff.) required for diffusion has been applied in place of $\Delta F_{\ddagger}^{\ddagger}$rearr..

The electrostatic energy barrier the electron has to overcome is lowered owing to (i), so the transition probability increases. By this the 'defect' observed by Eyring and his co-workers to be 8·1 kcal./mole is somewhat decreased.

[20] Z. V. Shpolskii, 'Atomnaia fizika', Moscow, 1951, p. 431.
[21] J. E. B. Randles, *Trans. Faraday Soc.*, 1952, 48, 828.
[22] J. Weiss, *Proc. Roy. Soc.*, 1954, A, 222, 128.
[23] K. J. Laidler. *Canad. J. Chem.*, 1959, 37, 138.

Laidler carried out calculations for the experimentally best known Fe^{II}–Fe^{III} reaction only. The results are exactly the same as the experimental values. This agreement is unique, but the assumptions cannot be accepted. The discarding of the Franck–Condon restriction means, in fact, that the electron is in a steady 'dispersed' state with a decreasing amplitude defined by the tunnel effect, in continuous 'readiness' for exchange around the reducing ion and the oxidising ion is permanently able to accept this electron. All the other portions of activation energy serve only to bring the reactants closer to one another. From this it follows (as an extreme case) that a crystal composed of such aquated or complex ions should show metallic conductance. This, however, could not be expected since, for example, Prussian blue is a semiconductor, *i.e.*, the charge-transfer process is appreciably hindered.

Later[24] the model was corrected by the rearrangement of the environment and the diffusion term was omitted. In this form the model is similar to those in the following section with the only difference that tunneling has been retained.

(ii) *Calculation of energy relations of the activated complex by polarisation.* The theory most frequently quoted is that of Marcus.[25] His model is fundamentally an electrostatic concept too. It is to be considered as a great advance, however, that all parts of the activation free energy can be calculated *a priori*. Moreover, this is the first theory suitable for deducing quantitative relations for redox reactions, and for discussion of the rate of electro-chemical and chemical reactions by identical principles.

The model is as follows: ions are considered to be metal spheres of radius r_0. Around them there is a solvent (or ligand) layer of thickness $a_0 - r_0$ assumed to be dielectrically saturated. The solvent outside this sphere of radius a_0 is taken as a continuous medium with dielectric constant D_s.

In the activated complex the two spheres of $a_{o,n}$ and $a_{o,m}$ radii are in contact. Unlike the previous theories, the tunnelling probability is estimated to be around unity owing to the high value of p, so there is no need of free energy for the *spatial* transfer of the electron. Free-energy requirements show up in Coulomb repulsion, and in the so-called 'non-equilibrium' polarisation. This renders it possible to calculate the energy required to fulfil the Franck–Condon principle in a classical way avoiding the difficult problems of quantum mechanical treatment. For in chemical reactions, taking place by transition of an atom or a group of atoms, the electronic orbitals in the activated complex overlap to a great extent, while for electron-transfer reactions smaller interactions and orbital overlaps are expected. The interaction of the reacting ion pair is thus probably smaller than or about the same as that of the ions and the environment or of the activated complex and the environment. Thus, while in the calculation of other reactions the interaction of partners and the solvent can be taken to be in equilibrium, for electron transfers this assumption is not allowed.

[24] K. J. Laidler and E. Sacher, 'Modern Aspects of Electrochemistry', Butterworths, London, 1964, vol. 3, pp. 1–42.
[25] R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966; *ibid.*, 1957, **26**, 867; *Canad. J. Chem.*, 1959, **37**, 155; *Discuss. Faraday Soc.*, 1960, **29**, 21; *J. Phys. Chem.*, 1963, **67**, 853; *J. Chem. Phys.*, 1965, **43**, 679.

On the other hand, the electron transfer is extremely fast. The new charge distribution, affected in the activated complex, can be followed only by the electronic polarisation among the different parts (atomic, orientation, and electronic) of the dielectric polarisation of the environment, since the other two would involve nuclear displacement. That is, the non-equilibrium state of the neighbouring solvent at the moment of the electronic jump arises from the inertness of the 'heavy' nuclei.

Since detailed calculations are tedious, only the final results can be reported here. Marcus estimated the slowest elementary step to be the collision in a suitable polarised arrangement of the water molecules. Therefore the rate constant is given by equation (4), where Z is the number of collisions, while the activation

$$k = Z \exp \left(-\frac{\Delta F^*}{RT} \right) \tag{4}$$

free energy is:

$$\Delta F^* = m^2 \lambda + \frac{z_n z_m}{D_s r_{n,m}} \tag{5}$$

where

$$m = -\frac{\Delta F^\circ + \dfrac{z_{n,t} \, z_{m,t} \, - z_n z_m}{D_s r_{n,m}}}{2\lambda} - \frac{1}{2} \tag{6}$$

and

$$\lambda = \left(\frac{1}{2a_n} + \frac{1}{2a_m} - \frac{1}{r_{n,m}} \right) \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right) (\Delta z)^2 \tag{7}$$

In these equations D_s is the statical dielectric constant, D_{op} is the square of refraction index; $z_{n,t}$ and $z_{m,t}$ are the charges of the products, and Δz is the charge corresponding to the transferring electrons, while ΔF° is the standard free energy of the reaction. (The thermodynamic quantities with asterisks are not identical with those of sign ‡, because of the appreciable difference between kT/h and Z.) Since the reaction is the fastest at the smallest $r_{n,m}$, we have equa-

$$r_{n,m} = a_n + a_m \tag{8}$$

tion (8). Results so calculated are not in satisfactory agreement with the experimental values (Table 2). Calculating the size of the reacting spherical ions, Marcus considered the first co-ordination spheres of the ions to be unaltered by the electron transfer, only the polarisation free-energy change outside the first layer of the solvent being applied. This seems to cause merely the overestimation of rates (Table 2).

By further refinement of the model Hush between 1957 and 1959,[26] as well as

[26] N. S. Hush: *Z. Electrochem.*, 1957, **61**, 734; *J. Chem. Phys.*, 1958, **28**, 962; *Trans. Faraday Soc.*, 1961, **57**, 557.

Table 2

Reaction	$\Delta F\ddagger$ (kcal./mole)	
	(Calc.)	(Obs.)
$MnO_4^{2-}-MnO_4^{-}$	9·2	12·8[a]
$Fe(CN)_6^{4-}-Fe(CN)_6^{3-}$	10·1	12·7[b]
$Mo(CN)_8^{4-}-Mo(CN)_8^{3-}$	9·5	<12·6[c]
$Fe^{2+}-Fe^{3+}$	9·8	16·3[d]
$Co^{2+}-Co^{3+}$	9·9	16·4[e]

[a] J. C. Sheppard and A. C. Wahl, *J. Amer. Chem. Soc.*, 1953, **75**, 5133. [b] A. C. Wahl and C. F. Deck, *J. Amer. Chem. Soc.*, 1954, **76**, 4054. [c] R. L. Wolfgang, *J. Amer. Chem. Soc.*, 1952, **74**, 6144. [d] See Ref. 32. [e] N. A. Bonner and J. P. Hunt, *J. Amer. Chem. Soc.*, 1952, **74**, 1866.

Marcus in 1960 introduced an additional term into the expression of free energy of activation which refers to changes in bond strength between the central ion and the water molecules just next to it. For transition-metal ions, as Hush assumed, this change in energy consists of two portions: (i) the 'pure' electrostatic interaction term due to the attraction between the central charge and the dipoles, and (ii) the crystal-field stabilisation energy change corresponding to the ligand–electron and electron–electron interactions. The first portion has been estimated to be small, *ca.* 2 kcal./mole, while the second one is significant, about 5 kcal./mole. For non-transition metals only the first one operates. The values calculated in this way fit far better the experimental ones than those of Marcus as shown in Table 3.

Table 3

Reaction	$\Delta H\ddagger$ (kcal./mole)		$\Delta S\ddagger$ (e.u.)	
	(Calc.)	(Obs.)	(Calc.)	(Obs.)
$Fe^{3+}-Fe^{2+}$	10·8	9·9[a]	−32	−25[a]
$V^{3+}-V^{2+}$	7·5	13·2[b]	−31	−25[b]
$Ce^{4+}-Ce^{3+}$	6·8	7·7[c]	−45	−40[c]
$NpO_2^{2+}-NpO_2^{+}$	9·6	8·3[d]	−19	−24[d]

[a] See Ref. 35. [b] K. V. Krishnamurty and A. C. Wahl, *J. Amer. Chem. Soc.*, 1958, **80**, 5921. [c] See Ref. *f* in Table 1. [d] D. Cohen, J. C. Sullivan, and J. C. Hindman, *J. Amer. Chem. Soc.*, 1956, **78**, 1540.

Returning to Marcus's theory, for the rate constant of redox reactions $k_{1,2}$, we can write equation (9) where $k_{1,1}$ and $k_{2,2}$ are the rate constants of the

$$k_{1,2} = \sqrt{(k_{1,1} k_{2,2} K_0 f)} \tag{9}$$

corresponding electron exchange reaction of the reactants, K_0 is the equilibrium constant, and

$$\ln f = \frac{(\ln K_0)^2}{4 \ln \dfrac{k_{1,1} k_{2,2}}{Z^2}} \tag{10}$$

If $\ln f$ is negligible and for similar systems for which $k_{1,1}$ and $k_{2,2}$ do not alter much on going from one system to another, one can expect the relation (11) to be valid, where a is a constant.

$$\ln k_{12} = a + \tfrac{1}{2}\ln K_0 \tag{11}$$

The validity of equation (11) was observed by Sutin and his co-workers investigating the oxidation of ferrous phenanthroline derivatives by cerium(IV)[27] and other reactions[28] (Figure 3). Some other observations[29] on exchange between
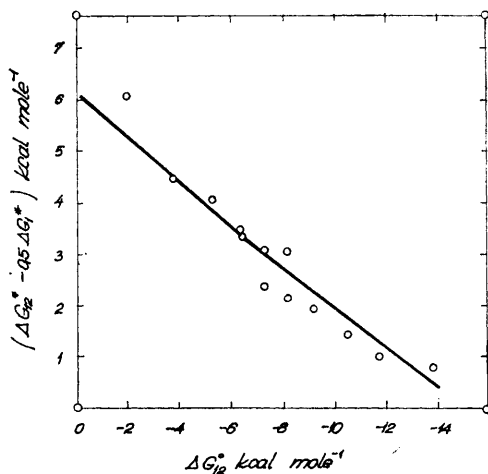

Figure 3 *Experimental results confirming the relation in equation* (11). *The circles correspond to reactions between cerium*(IV) *and various substituted iron*(II) *phenantrolines and between iron*(II) *and iron*(III) *phenantroline derivatives* (Reproduced from *Inorg. Chem.*, 1963, **2**, 917 by permission)

ferrous and ferric complexes show similar relations, but with respect to the absolute value of $\ln K_0$, the reason of which is not explained.

The essential identity of the processes of electrochemical and chemical electron-transfer reactions prompts one to find a relationship between the rates of the two kinds of reaction. Marcus's theory was the first suitable one for this.

If equations (5)—(7) are rearranged corresponding to electrochemical reactions, we get equation (12), where ΔF^*_c is the activation free-energy change

$$\Delta F^*_c \leqslant 2\Delta F^*_{el} \tag{12}$$

of the electron-exchange reaction, while ΔF^*_{el} is that of the reaction corresponding to the exchange current. The factor 2, in fact, means that two particles (and their co-ordination sphere) participate in the chemical reaction, while in

[27] G. Dulz and N. Sutin, *Inorg. Chem.*, 1963, **2**, 917.

[28] R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, 1964, **3**, 1091.

[29] K. Bäckmann and K. H. Lieser: *Ber. Bunsenges. Phys. Chem.*, 1963, **67**, 802; 1963, **67**, 810; *Z. phys. Chem.*, 1963, **36**, 236; Symp. on Exchange Reactions, Upton, 1965, Paper SM-64/10.

electrode reactions only one do so. If polarisation processes in the adsorption layer of the electrode are not negligible, the equality sign must be replaced by $<$. From equation (12) we have equation (13) where Z_c is the collision number of

$$\sqrt{\left(\frac{k_c}{Z_c}\right)} \geqslant \frac{k_{el}}{Z_{el}} \tag{13}$$

the chemical reaction (*ca.* 10^{11} mole^{-1} sec.$^{-1}$), while Z_{el} is that of the electrochemical one (*ca.* 10^4 cm. sec.$^{-1}$). Thus k_{el} calculated on the basis of the exchange-current values can be compared with the rate constant of the electron-exchange reaction (Table 4). Values show good agreement thereby proving the identity of the fundamental processes.

Table 4

System	$\sqrt{(K_c/10^{11})}$	$K_{el}/10^{4a}$
$Fe(CN)_6{}^{4-}$–$Fe(CN)_6{}^{3-}$	1×10^{-3b}	1×10^{-5}
$MnO_4{}^{2-}$–$MnO_4{}^{-}$	2×10^{-4c}	7×10^{-7}
Fe^{2+}–Fe^{3+}	9×10^{-6d}	7×10^{-7}
V^{2+}–V^{3+}	4×10^{-7e}	4×10^{-7}
Eu^{2+}–Eu^{3+}	6×10^{-8f}	3×10^{-8}
Tl^{+}–Tl^{3+}	3×10^{-8g}	2×10^{-8}
$Co(NH_3)_6{}^{2+}$–$Co(NH_3)_6{}^{3+}$	$<5 \times 10^{-11h}$	5×10^{-12}

[a] J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, 1952, **48**, 937. [b] A. C. Wahl, *Z. Electrochem.*, 1960, **64**, 90. [c] See Ref. *a* in Table 3. [d] See Ref. 32. [e] K. V. Krishnamurty and A. C. Wahl, *J. Amer. Chem. Soc.*, 1958, **80**, 5921. [f] D. J. Meier and C. S. Garner, *J. Phys. Chem.*, 1952, **56**, 833. [g] E. Roig and R. W. Dodson, *J. Phys. Chem.*, 1961, **65**, 2175. [h] See R. A. Marcus's explanation in *J. Phys. Chem.*, 1963, **67**, 853.

An essentially similar model has been used, but computed elegantly on quantum mechanical basis, by Levich and his co-workers.[30,31] Their theory was outlined first for electrode reactions. The approximations, differing in their mathematical nature from those of Marcus, led to somewhat different results, although in the classical limit the formulae fit Marcus's ones. They used also a continuous dielectric medium but, because of the complexity of the problem, they had to neglect the effect of the inner co-ordination sphere.

As has been pointed out, all the theories based on the polarisation approach attribute a marked influence to the environment outside the first co-ordination sphere. This leads to a prediction that the rate of electron-transfer reactions should depend on the dielectric constant of the medium [see, *e.g.*, equations (5)—(7)]. Some investigations in mixed solvents, however, do not confirm this relation:[32,33] the rate is essentially independent of the macroscopic dielectric

[30] V. G. Levich and R. R. Dogonadze, *Doklady Akad. Nauk S.S.S.R.*, 1959, **124**, 123; 1960, **133**, 158.
[31] R. R. Dogonadze: *Doklady Akad. Nauk S.S.S.R.*, 1960, **133**, 1368; R. R. Dogonadze and Y. A. Chizmadzhev, *ibid.*, 1962, **144**, 1077.
[32] D. Cohen, J. C. Sullivan, E. S. Amis, and J. C. Hindman, *J. Amer. Chem. Soc.*, 1956, **78**, 1543.
[33] R. A. Horne, Symp. on Exchange Reactions, Upton, 1965, Paper SM-64/18.

properties of the solvent in a broad range of D. The solvent component of lower dielectric constant does not affect the reaction as far as the selective solvation of the component of higher D is not disturbed.

On the other hand, these theories predict usually negative entropy of activation. In several cases, however, a positive entropy change has been measured that cannot be interpreted on the basis of polarisation theory.

B. Theories in which Indirect Electron Transfer is Assumed.—(i) *Hydrogen-atom transfer.* In the investigation of electron-transfer reactions the pH-dependence of the rate has been observed for many reactions. In the rate law, however, no integer was directly measured as the order of hydrogen ion concentration. By expansion, used in such cases, a variety of reaction orders have been obtained for the different reactions. For example, the $Fe^{2+} - Fe^{3+}$ exchange could be

$$k = a + \frac{b}{[H^+]} \tag{14}$$

described[34] by a rate constant (14), where a and b are constants.

To interpret the pH-dependence, it was assumed that the reaction path changing with acidity corresponds to electron transfer between metal ions hydrolysed to varying extents. Thus the Fe^{II}–Fe^{III} electron exchange can take place *via* two paths: either by the reaction of $Fe(H_2O)_6{}^{2+}$ with $Fe(H_2O)_6{}^{3+}$, or of $Fe(H_2O)_6{}^{2+}$ with $Fe(H_2O)_5OH^{2+}$.

Dodson and his co-workers[35,36] conceived the activated complex of the second reaction as in (II). According to them, electron transfer proceeds with the simul-

$$(H_2O)_5Fe^{II}\text{---}O\text{---}H \ \ldots \ldots \ O\text{---}Fe^{III}(H_2O)_5$$
$$\vert \qquad\qquad\qquad \vert$$
$$H \qquad\qquad\qquad H$$

(II)
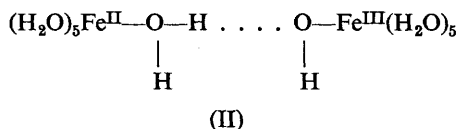
taneous vibration of the proton forming the bridge which really means the transition of a hydrogen atom.

Amis[9] tried to treat quantitatively a similar model, namely the acid-catalysed Np^V–Np^{VI} exchange. Applying the procedure of Eyring and his co-workers he calculated the transfer probability χ_e through a double potential barrier which is seen in Figure 4. However, the value of $8\cdot1$ kcal./mole for $\Delta F\ddagger_{rearr.}$ used by Eyring *et al.* seemed to be too large, since it would result in an unbelievably large value for the Bohr radii of the electron in the corresponding ions. To obtain reasonable results, the rearrangement free energy had to be lowered to about -4 kcal./mole, but this is inconsistent with the Franck–Condon restriction. These contradictions may be caused by the rough approximations in the calculation, whereas Dodson's model is fundamentally correct. Reynolds and

[34] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, 1951, **56**, 846.

[35] R. W. Dodson and N. Davidson, in the discussion of Ref. 11.

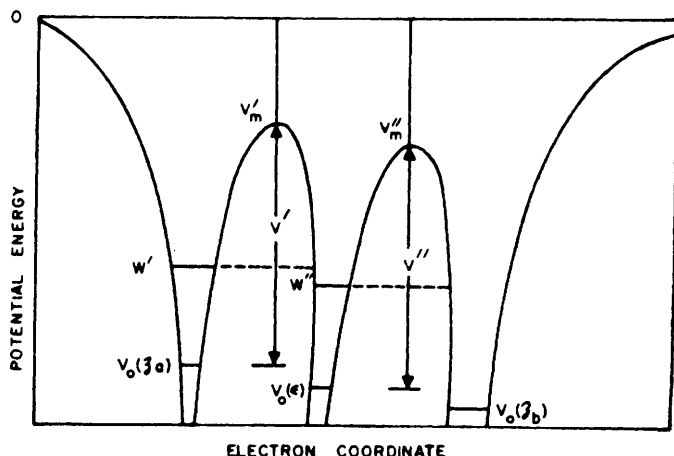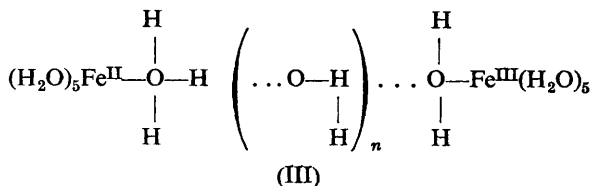[36] J. Hudis and R. W. Dodson, *J. Amer. Chem. Soc.*, 1956, **78**, 911.

Figure 4 *Double potential barrier for the* NpO_2^+–H^+–NpO_2^{2+} *activated complex* (Reproduced from E. S. Amis, 'Solvent Effects on Reaction Rates and Mechanisms', Academic Press, Inc., New York, 1966, p. 110 by permission)

Lumry[37] supposed the hydrogen ion to play a much more extended rôle. They consider *all* electron transfers to proceed through an activated complex as in (III).

$$
(H_2O)_5Fe^{II}\!\!-\!\!\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{O}}}}\!\!-\!\!H \quad \left(\ldots\overset{\displaystyle}{\underset{\displaystyle H}{\overset{}{\underset{|}{O}}}}\!\!-\!\!H\right)_n \ldots \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{O}}}}\!\!-\!\!Fe^{III}(H_2O)_5
$$

(III)

This theory suggests that acid-catalysis should be observed for electron-transfer reactions, since protonated Fe^{2+} ion is found at the left-hand end of the above chain. Such a phenomenon was observed for only a few reactions, so the mechanism did not seem generally valid.

It is known that the mobility of H^+ and OH^- ions is greater by an order of magnitude in water than that of other ions. This can be explained by Grotthus's concept[38] that the 'excess' and 'missing' protons of the H_2O^+ ion and OH^- ion, respectively, run through the chain of water molecules like a polarisation wave. Horne and Axelrod,[39] renewing Reynolds and Lumry's assumption, attribute the mobility of 'hydrogen atom' to this mechanism. This has been said to be proved by the fact that the enthalpy and entropy of activation for the Fe^{2+}–Fe^{3+} electron exchange in ice was the same as in aqueous solution.[40]

[37] W. L. Reynolds and R. Lumry, *J. Chem. Phys.*, 1955, **23**, 2560.
[38] C. J. T. Grotthus, *Ann. Chim.*, 1806, **58**, 54.
[39] R. A. Horne and E. H. Axelrod, *J. Chem. Phys.*, 1964, **40**, 1518.
[40] R. A. Horne: *J. Inorg. Nuclear Chem.*, 1963, **25**, 1139.

Concentrations used were such (*ca.* 10^{-3}M) that the ions were placed at an average distance of *ca.* 100 Å. Under these conditions, the electron had to pass through a layer of about 30 water molecules to reach the ion in the oxidised state.

Horne and Axelrod also assume that the total activation energy need of the reaction is consumed to form the chain of water molecules suitable to 'transport' the H atom. Thus energy is to be provided to produce the spatial arrangement of the water molecules of the chain. Obviously this energy is largely independent of the nature of the reactants (*ca.* 9·8—12·3 kcal./mole). The activation energies of the Fe^{II}–Fe^{III} exchanges are apparently in agreement with this value (8—10 kcal./mole), but results obtained for the activation energies of other reactions do not agree with this, suggesting that the agreement is probably accidental.

The most striking discrepancy is, however, that the changes in the electronic energy throughout the transfer are not taken into account. It is evident that the electronic energy, *e.g.*, at an Fe^{2+} ion is not identical with that of the solvated hydrogen atom. If electronic excitation is required in addition to the 9—10 kcal./mole due to the suitable rotation, how can such a low energy of activation be explained as the 4·6 kcal./mole value for the $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$ exchange? Further contradiction exists concerning acid catalysis, since this hypothesis also requires an H_3O^+ ion to transmit.

Recently Sykes[41] pointed out that a hydrated electron cannot exist as intermediate in electron-transfer reactions, since the rate law for a reaction sequence such as (15), (16) is given by (17). This rate law is valid as far as the steady-state

$$Cr^{II} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr^{III} + e_{aq} \tag{15}$$

$$Fe^{III} + e_{aq} \overset{k_2}{\longrightarrow} Fe^{II} \tag{16}$$

$$-\frac{d[Fe^{III}]}{dt} = \frac{k_1 k_2 [Fe^{III}][Cr^{II}]}{k_{-1}[Cr^{III}] + k_2[Fe^{III}]} \tag{17}$$

treatment is allowed to be used, that is, as far as the transferring charge can become independent in movement from the ion yielding it. Thus, other things being equal, it must be true for the Horne-Axelrod mechanism. Neither this rate law, nor its limiting cases have been observed so far.

(ii) *The 'band model'.* Recently a new theory was published by Ruff[42] based, in part, on the former concepts of indirect electron transfer, but eliminating the contradiction within the assumptions and pointing to their extended applicability for both inner and outer sphere mechanisms.

The fundamental supposition of this theory is connected with the question: what is the intermediate 'H atom' like? Reynolds and Lumry as well as Horne

[41] A. G. Sykes, 'Kinetics of Inorganic Reactions', Pergamon Press, 1966, p. 222.
[42] I. Ruff, *J. Phys. Chem.*, 1965, 69, 3183; *Acta Chim. Acad. Sci. Hung.*, 1966, **47**, 245; 1966, **47**, 255; 1967, **52**, 251.

and Axelrod speak of hydrogen atom as if it were a hydrogen atom as it would be in a gaseous phase, but immersed in water without any alteration. This could not serve as a transporting particle, since it could not move by a Grotthus mechanism, because its proton would not take part in any hydrogen bonding. On the other hand, if it is an H_3O radical, which is a reasonable assumption, its life time (*ca.* 10^{-9} sec.[43]) does not seem to permit its moving apart from its original position more or less close to the electron-donor ion. It can mediate the transfer, however, in such a fixed state if the electron cloud of H_3O is widely spread. This can be expected to be so, for the charge of the H_3O^+ ion itself, being the 'nucleus' of the quasi-hydrogen atom, is spread over several water molecules, and the wave function of the electron ordered around this charge must be highly extended in space. By the usual treatment for similar problems, the Bohr radius of such a 'hydrogen atom' has been estimated to be around 40 Å. This value is of the same order of magnitude as the radius of impurity wave functions in semiconductors in which the dielectric constant is smaller but the effective mass for the electron is taken. It is noteworthy that Amis's treatment led to a similarly large value, but whether this is due to the nature of the problem or to errors in approximations is not known.

Thus, H_3O^+ can serve as a bridge for the transferring electron if its wave function covers both of the reacting ions, *i.e.*, even if they are so far apart as 80 Å. Further, the hydroxonium ion is not required to be either in the *close* vicinity of the reducing ion or *between* the reacting ions at the moment of the electronic excitation. The only restriction is that both ions must be inside the effectivity space of the H_3O radical.

The other feature of the H_3O radical is that the energy of the electron, bound to it, is appreciably higher than that of any of the reactant ions. If not, the water would decompose. It has been shown that these energies can be calculated by the normal oxidation–reduction potentials of the corresponding ions and so at least the difference between the potentials due to the process $H_3O^+ + e^- \rightleftharpoons H_3O$ and $M^{n+} + e^- \rightleftharpoons M^{(n-1)+}$ must be supported as activation energy.

The electron transfer takes place *via* two steps (18) and (19). If it is assumed

$$M_1^{(n-1)+} + H_3O^+ \rightarrow M_1^{n+} + H_3O \tag{18}$$

$$M_2^{m+} + H_3O \rightarrow M_2^{(m-1)+} + H_3O^+ \tag{19}$$
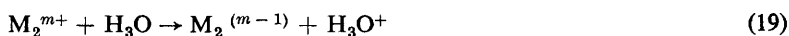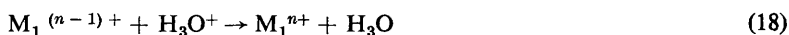
that H_3O does not move apart from M_1^{n+}, *i.e.*, it is not an independent particle, Sykes's steady-state equation mentioned above should not be valid in this case.

There is another possible way [(20), (21)], very similar to the former one,

$$M_2^{m+} + OH^- \rightarrow M_2^{(m-1)+} + OH \tag{20}$$

$$M_1^{(n-1)+} + OH \rightarrow M_1^{n+} + OH^- \tag{21}$$

where the reaction starts on the oxidising ion by electron acceptance and the

[43] T. J. Sworski, *Adv. Chem.*, 1965, **40**, 263.

intermediate particle is an OH radical. Every statement that has been written in connection with the H_3O radical is true of this mechanism.

Representing the possible states of the transferring electron as a function of the position co-ordinate, and mark-in the extension of the corresponding electron clouds with the length of the horizontal lines due to the stationary levels (Figure 5), we can draw two approximately rectangular potential barriers
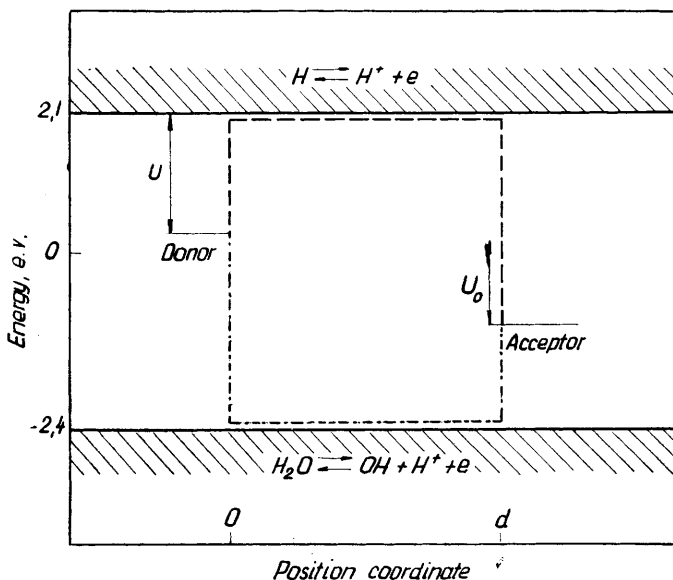

Figure 5 *Energy levels corresponding to the band model*

(broken lines). The upper one should be overcome in reaction (18), when, in fact, electron transfer takes place, and the lower, reversed barrier hinders the reaction (20) in which electron deficiency, *i.e.*, a hole is transferred. The reactant levels in electron-exchange reactions are identical in energy ($U_0 = 0$). The level of the reducing ion is occupied and that of the oxidising ion is unoccupied. For oxidation–reduction reactions the energy difference between the donor and acceptor level corresponds to that between the normal oxidation–reduction potentials of the reducing and oxidising ions, respectively.

This model is very similar to the band model of semiconductors, the electron and hole transfer paths being analogous to the *n* and *p* type conduction, respectively, with the only exception that the H_3O and OH states are not infinitely extended all over the system but only relatively with respect to the reactant distance.

Two further possible reaction paths exist, if one presumes tunnelling: one through the upper barrier by electron tunnelling and another by hole tunnelling. Tunnelling occurs when the energy of activation is not enough for a 'classical' transfer above the barrier. Among the four possible paths that one will be

215

favoured which requires the smallest free energy of activation. We shall turn now to the quantitative relationships based on this model.

It has been shown that the entropy of activation can be calculated by equations

$$\Delta S_{\ddagger}^{\ddagger} = \Delta S_{t\ddagger}^{\ddagger} + \Delta S_{i\ddagger}^{\ddagger} + \Delta S_{e\ddagger}^{\ddagger} - R \tag{22}$$

$$\Delta S_{e\ddagger}^{\ddagger} = R \ln p_{e} \tag{23}$$

$$\Delta S_{i\ddagger}^{\ddagger} = R \sum_{i} \ln p_{i} \tag{24}$$

$$\Delta S_{t\ddagger}^{\ddagger} = -2R \ln c_{*} \tag{25}$$

(22)—(25). Here p_e is the transition probability of the electron, p_i is the probability of satisfaction of the ith configurational requirement of the activated complex ($\Delta S_{i\ddagger}^{\ddagger}$ represents that fraction of the collisions which take place at a favourable orientation), and c_* is the so-called normalised concentration, *i.e.*, at this concentration the average distance between the reactants in solution is equal to the distance d between the reactants in the activated complex and is given by equation (26) where N is Avogadro's number. $\Delta S_{t\ddagger}^{\ddagger}$ represents the

$$c_{*} = (10^{-3} d N)^{-1} \tag{26}$$

entropy due to the change in the degrees of freedom of translation.

In the case of transfer above the barrier the activation energy is larger or equal to U, but then we have $p_e = 1$ if the reactants are situated inside the effectivity space of one H_3O or OH radical. If we consider their above-mentioned Bohr radii, this means that the reactants should approach one other at least to about 80 Å. Thus, on the basis of equations (22)—(26), equation (27) follows, since

$$\Delta S_{\ddagger}^{\ddagger} = 21 \text{ e.u.} \tag{27}$$

for the outer-sphere mechanism the reactants can be considered to be spheres, *i.e.*, there is no configurational restriction for the collision either.

It has been an important result of this theory that it could explain the positive entropy of activation observed. The calculated value is compared with the experimental ones in Table 5 below the broken line. In view of the rough approximations, the agreement is quite satisfactory. All reactions listed in Table 5 proceed by hole transfer, because the level of their oxidising reactivity is very near the lower energy limit (see Figure 5). Equation (20) shows that the rate of such hole transfers above the barrier should be a linear function of OH^- concentration, *i.e.*, the rate law should involve the reciprocal of the hydrogen-ion concentration. This pH-dependence should not be due to hydrolysis, as was supposed in the original papers.

The present theory predicts base catalysis, unlike the former models for indirect transfer which would require acid catalysis in contradiction with experiments. Acid catalysis would appear in electron transfer above the barrier, but this path would be favoured only in systems containing extremely strong reducing agents.

In the case of the tunnel effect the fastest path corresponds to the minimum d.

Table 5

Reaction	$\Delta S^{\ddagger}_{+\text{calc.}}$ (e.u.)	$\Delta S^{\ddagger}_{+\text{obs.}}$ (e.u.)	[H$^+$]-order
	Hole transfer reactions		
$Np^{VI}-Np^{V}$	-20	-24^b	$+1$
$Fe^{III}-Fe^{II}$	-23	-25^c	0
$Mn^{VII}-Mn^{VI}$	-16	-16^d	0
$Fe(CN)_6{}^{3-}-Fe(CN)_6{}^{4-}$	-21	-21^d	0
$V^{IV}-V^{III}$	-26	-24^e	-1
$Ce^{IV}-Ce^{III}$	21	25^f	-2
$Co^{III}-Co^{II}$	21	$21^g; 27^h$	-1
$Co^{III}-Fe^{II}$	21	11^i	-1
$Co^{III}-Ce^{III}$	21	14^j	-1
$Co^{III}-Tl^{I}$	21	22^k	-1
$Np^{VI}-V^{III}$	21	19 ± 10^l	-1
	Electron transfer reactions		
$V^{II}-V^{III}$	-28	-25^m	0
$Co(NH_3)_6{}^{2+}-Co(NH_3)_6{}^{3+}$	-32	-41^n	0
$Co(en)_3{}^{2+}-Co(en)_3{}^{3+}$	-32	-33^p	0
$Co(EDTA)^{2-}-Co(EDTA)^{-}$	-23	-17^q	0^a
$Ce^{III}-Ce^{IV}$	-37	-40^f	0

[a] pH dependence due to equation (30). [b] See Ref. *d* in Table 3. [c] See Ref. 35. [d] See Ref. *b* in Table 4. [e] See Ref. *d* in Table 1. [f] See Ref. *f* in Table 1. [g] J. Shankar and B. C. de Souza, *J. Inorg. Nuclear Chem.*, 1963, **24**, 693. [h] H. S. Habib and J. P. Hunt, *J. Amer. Chem. Soc.*, 1966, **88**, 1668. [i] L. E. Bennett and J. C. Sheppard, *J. Phys. Chem.*, 1962, **66**, 1265. [j] L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, 1956, **52**, 1225. [k] J. Halpern, *Canad. J. Chem.*, 1959, **37**, 148. [l] J. C. Sheppard, *J. Phys. Chem.*, 1964, **68**, 1190. [m] See Ref *b* in Table 3. [n] N. S. Biradar, D. W. Stransk, M. S. Vaidhya, G. J. Weston, and D. J. Simpson, *Trans. Faraday Soc.*, 1959, **55**, 1268. [p] See Ref. *b* in Table 1. [q] A. W. Adamson and K. S. Vones, *J. Inorg. Nuclear Chem.*, 1956, **3**, 203.

For the outer sphere mechanism this was assumed to occur by the penetration of the second co-ordination spheres, leading to a value of d about 9·4 Å, from which it follows that $\Delta S^{\ddagger}_{t\ddagger} \approx 0$. On the basis of the Gramow equation (28) the

$$p_e = \exp\left(-\frac{4\pi}{h}\,d\,\sqrt{[2m\,(U\text{-}E_a)]}\right) \tag{28}$$

total entropy of activation is given by (29), since spherical symmetry is valid in

$$\Delta S^{\ddagger}_{\ddagger} = -R\,\frac{4\pi}{h}\,d\sqrt{[2m(U\text{-}E_a)]} - R \tag{29}$$

this case too.

Almost all the observed entropies of activation for electron exchange reactions are summarised in Table 5. The comparison seems to prove the applicability of this model. A slightly worse, though satisfactory, fitting has been observed for oxidation–reduction reactions. As tunnelling probability is independent of the

height of the acceptor level, the entropy of activation can be calculated by equation (29) for both electron exchange and oxidation–reduction reactions. This contradicts the result in Marcus's theory [equation (9)], but it arises from the approximation used for tunnelling; that is, the changes in the barrier height caused by the overlap of the donor and acceptor levels cannot be allowed for by tunnelling, but by the appropriate individual electronic orbitals which would be extremely difficult to calculate. For the tunnelling paths a slight pH-dependence can be expected; since the limit energies in Figure 5 vary linearly with pH,

$$\ln k = -a\sqrt{(U - E_a + 2.303\ kT\mathrm{pH})} + b \tag{30}$$

equation (30) can be obtained, where a and b are given by equations (31) and

$$a = \frac{4\pi}{h} d\sqrt{(2m)} = 7.6 \times 10^6\ \mathrm{g.}^{-\frac{1}{2}}\ \mathrm{cm.}^{-1}\ \mathrm{sec.}^{-1} \tag{31}$$

(32). The sign before the term $2.303\ kT\mathrm{pH}$ is positive for electron transfer and

$$b = \ln \frac{kT}{h} - \frac{E_a}{RT} \tag{32}$$

negative for hole transfer. Equation (30) fits the pH-dependence of the reactions between V^{II} and U^{VI}, Fe^{II} and H_2O_2, Pu^{VI} and Fe^{II}, and $Co^{III}EDTA$ and Co^{II}-EDTA, with slopes 1.3×10^6, 6.8×10^6, 13×10^6, and 9.7×10^6 respectively.

An important feature of this theory is that the electrostatic interactions have been neglected, because at the larger interionic distances supposed their effect is small. Thus, the energy of activation is due to the rearrangement of the inner co-ordination spheres. This has been estimated, by use of Van Vleck's formulae, by equation (22), where the terms of the right-hand side are the crystal field

$$E_a = (10Dq)_{ox} - (10Dq)_{red} \tag{33}$$

splittings of the (electron or hole) donor ion in its oxidised and reduced state, respectively. This is somewhat similar to Hush's treatment for estimating the crystal field stabilisation energy changes, but there a linear approximation has been used with respect to λ. Because the acceptor ion is far from the donor, it does not affect the excitation process, *i.e.*, the energy of activation is independent of the nature of the acceptor and of whether the actual path is electron or hole transfer. Some examples are shown in Table 6 which confirm this correlation. Equation (33) does not hold for the case when the electronic structure of the donor ion is much altered by the loss of the electron or hole, *e.g.*, when a high spin–low spin transformation takes place [$Co(en)_3^{3+} - Co(en)_3^{2+}$].

Unlike Marcus's theory, the results of this treatment for electrode reactions show that there should be no difference in the energy of activation between electrochemical and chemical electron-transfer reactions (see, *e.g.*, the values marked by 'electrode' in Table 6). The difference exists only in the entropy terms, since one ion may approach the electrode more easily than the other ion so that the tunnelling distance is decreased. Some calculated exchange current values are in good agreement with the measured ones.

Table 6

Change in oxidation number on the donor	Reaction partner	E_a (calc.) (kcal./mole)	E_a (obs.) (kcal./mole)
$V^{IV} \to V^{III}$	V^{III}	11·2	10·7[e]
$V^{II} \to V^{III}$	V^{III}	13·2	13·2[m]
$V^{II} \to V^{III}$	U^{VI}	13·2	7·3[α]
$V^{II} \to V^{III}$	$Co(NH_3)_6^{3+}$	13·2	9·7[β]
$V^{III} \to V^{II}$	Eu^{II}	13·2	12·0[γ]
$Fe^{III} \to Fe^{II}$	Fe^{II}	9·5	9·9[d]
$Fe^{II} \to Fe^{III}$	H_2O_2	9·5	9·4[δ]
$Fe^{III} \to Fe^{II}$	electrode	9·5	9[e]
$Co^{III} \to Co^{II}$	Co^{II}	24·6	21·6[g], 28·5[h]
$Co^{III} \to Co^{II}$	Fe^{II}	24·6	17·2[i]
$Co^{III} \to Co^{II}$	Ce^{III}	24·6	19·0[j]
$Co^{III} \to Co^{II}$	Tl^{I}	24·6	26·4[k]
$Fe(CN)_6^{3-} \to Fe(CN)_6^{4-}$	$Fe(CN)_6^{4-}$	—	4·6[d]
$Fe(CN)_6^{3-} \to Fe(CN)_6^{4-}$	electrode	—	4[e]
$Co(EDTA)^{2-} \to Co(EDTA)^{-}$	$Co(EDTA)^{-}$	26·1	22[q]
$Co(NH_3)_6^{2+} \to Co(NH_3)_6^{3+}$	$Co(NH_3)_6^{3+}$	64·0	13·5[n]
$Co(en)_3^{2+} \to Co(en)_3^{3+}$	$Co(en)_3^{3+}$	64·0	14·3[d]

For the references denoted by roman letters see the same letter in Table 5; [α] T. W. Newton and F. B. Baker, *J. Phys. Chem.*, 1965, **69**, 176. [β] A. Zwinkel and H. Taube, *J. Amer. Chem. Soc.*, 1961, **83**, 793. [γ] A. Adin and A. G. Sykes, *Nature*, 1966, **209**, 804. [δ] J. Sobkowski, *Roczniki Chem.*, 1961, **36**, 1503. [e] See Ref. *a* in Table 4.

4 Inner Sphere Mechanism

As has been noted, the *a priori* theoretical investigation of inner sphere electron-transfer reactions is more difficult owing to several complications which do not appear in outer sphere mechanism. These are: (i) the lack of spherical symmetry of the reactants in their collision, since they must collide in the direction of the bridging ligand; (ii) the close contact of the reactants that results in larger overlap in the electronic orbitals; (iii) the lower symmetry makes the calculation of the rearrangement free energy more difficult; (iv) the nature of the bridging ligand cannot be considered exclusively to be a point charge or dipole, but its electronic orbitals significantly influence the electron transfer.

These complications cause our knowledge of the inner sphere mechanism to be based primarily on conclusions of experiments reviewed elsewhere,[5,7] which fall outside our area of *a priori* theories. It is possible that some theoretical information may be obtained by a general quantum mechanical treatment, but this would yield only qualitative results, or by a simpler model like that of the outer sphere mechanism, which could at least estimate the kinetic parameters.

The quantum mechanical treatment, as outlined by Halpern and Orgel,[44]

[44] J. Halpern and L. E. Orgel, *Discuss. Faraday Soc.*, 1960, **29**, 32.

starts from the following assumptions: the energy conditions of the binuclear activated complex are entirely identical with those obtained by the Marcus theory except that the transfer probability of the electron, estimated to be about unity in the outer sphere case, is now much less and markedly regulated by the nature of the bridging ligand. On this basis the detailed mechanism of the electron transfer can be direct, double, and superexchange. Slightly vulgarising the question, one can say that direct exchange occurs, when the time for which the transferring electron is located on the bridging ligand is much less than that for which the electron is in its initial or final positions in the course of its oscillation between these. If not, double exchange appears, *i.e.*, the electron jumps first to the bridge and, after that, to the acceptor ion [equation (34)] or first from the

$$M_1L^-M_2^+ \rightarrow [M_1^+L^{--}M_2^+] \rightarrow M_1^+L^-M_2 \tag{34}$$

ligand to the acceptor, then from the donor to the ligand [equation (25)].

$$M_1L^-M_2^+ \rightarrow [M_1LM_2] \rightarrow M_1^+L^-M_2 \tag{35}$$
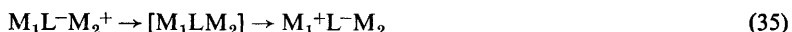
In superexchange the activated states in equations (34) and (35) are mixed

$$M_1L^-M_2^+ \rightarrow [M_1^+L^{--+}M_2] \rightarrow M_1^+L^-M_2 \tag{36}$$
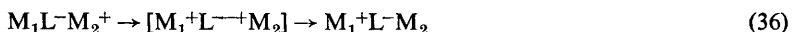
as in equation (36), that is, the hole starting from M_2 and the electron of M_1 are recombined at the ligand.

Halpern and Orgel emphasise the rôle of conjugation of the π electrons in organic bridging ligands and of the symmetry of the electronic orbitals in transition-metal ions as well. Conjugation is an accelerating effect owing to the high 'conductivity' of the bridge. The orbital symmetry of the transferring electron may affect the rate as follows: in the case of e_g and t_{2g} electrons, transfer *via* σ and π type molecular orbitals is favoured, respectively. Further on, the oxidation–reduction potential of the ligand is predicted to be important in the mechanism of superexchange. All these qualitative theoretical results are in excellent agreement with the measured rates of different bridged systems.

As can be seen, there is a high similarity between the double exchange mechanism represented by equations (34) and (35) and the electron and hole transfer paths in Ruff's theory. In this way the band model was extended recently to the inner sphere mechanism.[45] The simplified method of calculation of the transfer probability gives quantitative data for the entropy of activation. The approximate rectangular potential barrier in Figure 5 is lowered if the oxidation–reduction potential of the bridging ligand differs favourably from the corresponding limit potential; at the same time the barrier width becomes smaller owing to the reduced tunnelling distance in the bridged complex. In addition, the asymmetric behaviour of the reactants in collision should be taken into account. The entropy values, calculated in this way for halides as bridging ligands, are around -25 e.u. in good agreement with the measured ones.

[45] I. Ruff, *J. Phys. Chem.*, in the press.

5 Conclusions

Although the theories reviewed show essential differences in the model of electron-transfer reactions, it is clear that the grounds of the detailed mechanism are revealed. The phenomena affecting the rate of these processes are in general: (i) the collision of the reactants, (ii) the rearrangement of the environment, and (iii) the probability of the electronic jump. It is also obvious that an *ab initio* quantum mechanical treatment would be the most sophisticated theoretical approach but, even if its difficulties are disregarded, its results would be individual which is never the purpose of any theory. Thus, further development can be expected to be based on refinement of the approximations used so far, perhaps with a unification of the advantageous properties of the various theories; it will be desirable to retain general validity, since the purpose is to understand and explain the experimentally observed behaviour of oxidation–reduction reactions and not to replace measured values with calculated ones.