MECHANISMS OF ELECTRON TRANSFER AND RELATED PROCESSES IN SOLUTION

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THIS Review is concerned with the mechanisms of simple redox reactions in solution, notably those involving the transfer of one or more electrons between metal ions or complexes. While many such reactions, *e.g.*:

$$\mathrm{Cr^{II} + Co^{III} \rightarrow Cr^{III} + Co^{II}} \quad . \ . \ . \ . \ . \ . \ (1)$$

$$\mathrm{U^{IV} + 2Fe^{III} \rightarrow U^{VI} + 2Fe^{II}} \quad . \ . \ . \ . \ . \ . \ . \ (2)$$

$$\mathrm{Sn^{II} + Tl^{III} \rightarrow Sn^{IV} + Tl^{I}} \quad . \ . \ . \ . \ . \ . \ . \ (3)$$

are among the most familiar of inorganic and analytical chemistry, interest in them, until relatively recently, appears to have been largely confined to considerations of stoicheiometry and thermodynamics, and it is only during the last decade that their kinetics and mechanisms have received serious attention.

In addition to the stimulation provided by the general expansion of interest in inorganic chemistry during this period, the considerable progress which has been achieved in the study of electron-transfer mechanisms has been made possible in part by a number of specific experimental developments. Perhaps foremost among these is the introduction into common laboratory practice of a wide range of isotopic tracers. These have found application in detailed mechanistic studies and have opened up the possibility for the investigation, not only of ordinary redox reactions, but also of isotopic exchange reactions involving electron transfer between different oxidation states of the same element,† *e.g.*:

$$\mathrm{Fe^{II} + {}^{*}Fe^{III} \rightarrow Fe^{III} + {}^{*}Fe^{II}} \quad . \ . \ . \ . \ . \ . \ . \ (4)$$

$$\mathrm{MnO_4^{2-} + {}^{*}MnO_4^{-} \rightarrow MnO_4^{-} + {}^{*}MnO_4^{2-}} \quad . \ . \ . \ (5)$$

Such reactions have the advantage, in many instances, of being slower and hence more readily accessible to kinetic measurement, than those involving net chemical change, and of providing simpler models on which to base theoretical calculations. Their study has, therefore, received particular attention. The range of electron-transfer reactions whose kinetics

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†The earliest such study, of the isotopic exchange between $\mathrm{Pb^{II}}$ and $\mathrm{Pb^{IV}}$, was reported by Hevesy and Zechmeister in 1920 (*Ber.*, 1920, **53**, 410). The limited availability of isotopic tracers, however, precluded extensive work of this type until relatively recently. It is now also possible, although as yet only in rather special cases, with techniques such as electron spin resonance and nuclear magnetic resonance spectroscopy, to measure rates of electron-transfer reactions in which there is no chemical change, without resorting to isotopic labelling.

can be studied has also been greatly extended by the development of various techniques for measuring the rates of fast reactions: among these are flow techniques,[1,2] nuclear magnetic resonance[3] and electron spin resonance[4] spectroscopy and relaxation methods,[5] which have yielded measurements of rate constants up to 10^9 l. mole^{-1} sec.$^{-1}$. It is noteworthy, however, that by no means all the recent progress in this field is due to these newer developments. Along with them, and stimulated by them, the study of familiar reactions such as (1)—(3) by conventional kinetic methods has played, and continues to play, an important role.

The elucidation of the mechanisms of electron-transfer reactions presents problems of considerably greater difficulty and complexity than are suggested by the simplified equations by which we usually represent such reactions. Some of the questions which arise, and with which this Review will be concerned, relate to the following themes:

(i) The nature and sequence, if more than one, of the elementary steps which comprise the overall reaction. Connected with this is the question whether multiequivalent redox processes such as (2) and (3) occur in a single step or through successive 1-electron steps.

(ii) The detailed mechanisms of the elementary steps themselves, *e.g.*, the composition and configuration of the activated complex, the roles of ligands and solvent, etc.

(iii) The significance of atomic rearrangements accompanying the electron transfer. In this connexion it should be recognised that all electron-transfer processes in solution involve some atomic rearrangement. In some reactions, for example those involving the MnO_4^{2-}–MnO_4^- or Fe_{aq}^{2+}–Fe_{aq}^{3+} couples, these are relatively subtle, *i.e.*, small differences in the metal–ligand bond lengths and in the polarisation of the surrounding solvent, corresponding to the two oxidation states. In others, for example reactions involving the U^{4+}–UO_2^{2+} or $PtCl_4^{2-}$–$PtCl_6^{2-}$ couple, gross changes in the geometry and composition of the co-ordination shell occur.

(iv) The significance of the large variations (typical examples of which are to be found in Table 1) in rate and in $\Delta H\ddagger$ and $\Delta S\ddagger$ which are observed in series of related reactions in which the metal ions or ligands are varied.

In so far as the two themes can be conveniently separated the experimental evidence relating to the kinetics and mechanisms of electron-transfer reactions will be considered first, being followed by a discussion of some of the theoretical aspects of the subject. No attempt has been made at

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[1] Sheppard and Wahl, *J. Amer. Chem. Soc.*, 1957, **79**, 1020; Gjertsen and Wahl, *ibid.*, 1959, **81**, 1572.

[2] Gordon and Wahl, *ibid.*, 1958, **80**, 273.

[3] McConnell and Weaver, *J. Chem Phys.*, 1956, **25**, 307; Bruce, Norberg, and Weissman, *ibid.*, 1956, **24**, 473.

[4] (*a*) Ward and Weissman, *J. Amer. Chem. Soc.*, 1957, **79**, 2086; (*b*) Adam and Weissman, *ibid.*, 1958, **80**, 1518.

[5] Diebler, *Z. Elektrochem.*, 1960, **64**, 128.

complete coverage, particularly of the experimental subject matter; emphasis is placed rather on the discussion of typical systems, notably those which have been most extensively investigated and are best understood. More detailed treatments of certain aspects of the subject are to be found in earlier reviews by Zwolinski, R. J. Marcus, and Eyring,[6] Amphlett,[7] Basolo and Pearson,[8] Taube,[9] and Stranks.[10]

Mechanisms of Direct Electron Transfer

Although some electron-transfer reactions to be considered in a subsequent section occur through indirect mechanisms, the kinetic evidence in most cases, *i.e.*, a rate-law of the first order in each of the reactants, points to a direct reaction between the oxidant and the reductant through an activated complex involving both. Kinetic measurements in such cases serve to define the composition of the activated complex (apart from solvent participation) but not its detailed configuration. However, particularly in cases where the reactants contain no solvent ligands or where the reactants and/or products are substitution-inert, at least some features of the mechanism and of the structure of the activated complex may be inferred through studies of the type to be described. These have resulted in the recognition of at least two broad classes of mechanism, the so-called "outer-sphere" and "inner-sphere" (or bridged) types.* In the first of these, electron transfer occurs through the intact co-ordination shells of both metal ions; and, in the second, through a bridged intermediate in which the two metal ions are linked by a bridging ligand common to the co-ordination shells of both. The distinction between the two is not always sharp and many reactions cannot at this stage be assigned with certainty to either class.

Outer-sphere Reactions.—In reactions of this type, examples of which are listed in Table 1(A), electron transfer occurs through an "extended" activated complex in which the first co-ordination shell of each metal ion is presumably intact. The evidence for this type of mechanism is usually (*a*) a rate-law corresponding to an activated complex containing all the ligands in the first co-ordination shells of both metal ions, *e.g.*, $k[\text{Co en}_3^{2+}][\text{Co en}_3^{3+}]$, and/or (*b*) the demonstration that electron

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*Various designations have been employed to distinguish these two classes of reaction. For the second class, the designation "inner-sphere" is preferred to "bridged" because bridging may also occur in outer-sphere mechanisms. The terms "extended" and "compact" have also been used to designate the two types of activated complex.

[6] Zwolinski, Marcus, and Eyring, *Chem. Rev.*, 1955, **55**, 157.

[7] Amphlett, *Quart Rev.*, 1954, **8**, 219.

[8] Basolo and Pearson, "Mechanisms of Inorganic Reactions", John Wiley and Sons, Inc., New York, 1958, Chapter 7.

[9] (*a*) Taube in Emeléus and Sharpe, "Advances in Inorganic Chemistry and Radiochemistry," Academic Press Inc., New York, 1959, p. 1; (*b*) Taube, *Canad. J. Chem.*, 1959, **37**, 129.

[10] Stranks in Lewis and Wilkins, "Modern Coordination Chemistry", Interscience Publishers, Inc., New York, 1960, p. 78.

transfer is faster than substitution into the co-ordination shell of either metal ion, *e.g.*, the very rapid electron exchange between $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$, both of which undergo substitution only slowly. In such a case, the fact that the co-ordination shells of the metal ions remain intact during electron transfer may be confirmed by simultaneous isotopic labelling of both the metal ion and the ligands, but this is usually considered unnecessary.

TABLE 1. *Kinetic data: 1-electron-transfer reactions*[a]

Reaction	Temp.	k_{bi} (l. mole^{-1} sec.$^{-1}$)	$\Delta H\ddagger$ (kcal. mole^{-1})	$\Delta S\ddagger$ (e.u.)	Ref.
(A) Outer-sphere reactions					
Co^{2+}–Co^{3+} [b]	3·2	~1	(12·6)	(−13)	11
Co $phen_3^{2+}$–Co $phen_3^{3+}$	0	1·1	17	+ 4	12
Co en_3^{2+}–Co en_3^{3+}	25	5 × 10^{-5}	13·7	−33	13
$Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$	64·5	<10^{-8}	—	—	14
$Co(NH)_3)_n^{2+}$–$Co(NH_3)_5OH^{2+}$	64·5	5·4 × 10^{-2}	12·7	−33	14
,, –$Co(NH_3)_6^{3+}OH^-$	64·5	0·33	12·2	−35	14
,, –$Co(NH_3)_6^{3+}Cl^-$	64·5	4·4 × 10^{-2}	—	—	14
Cr^{2+}–$Co(NH_3)_6^{3+}$	25	9·0 × 10^{-5}	14·7	−30	15*b*
Cr $dipy_3^{2+}$–$Co(NH_3)_6^{3+}$	4	7·1	13·0	−10	15*a*
,, –$Co(NH_3)_5OH_2^{3+}$	4	6·5 × 10^2	—	—	15*a*
,, –$Co(NH_3)_5Cl^{2+}$	4	1·0 × 10^4	—	—	15*a*
,, –$Co(NH_3)_5Br^{2+}$	4	> 1·6 × 10^4	—	—	15*a*
MnO_4^{2-}–MnO_4^-	0	7 × 10^2	10·0	− 9	1
$IrCl_6^{3-}$–$IrCl_6^{2-}$	1	> 3 × 10^2	—	—	16
$Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$	4	~10^3	—	—	17
Fe $phen_3^{2+}$–Fe $phen_3^{3+}$	0	>10^5	—	—	18
Ferrocene–ferrocinium	−75	9 × 10^5	—	—	14
(B) Inner-sphere reactions					
Cr^{2+}–Cr^{3+} [b]	24·5	⩽ 2 × 10^{-5}	(21)	(− 8)	19
,, –$CrOH^{2+}$ [b]	24·5	0·7	—	—	19
,, –CrF^{2+}	0	2·6 × 10^{-3}	13·7	−20	20
,, –*cis*-CrF_2^+	0	1·2 × 10^{-3}	13	−24	21
,, –$CrCl^{2+}$	0	9	—	—	20
,, –$CrBr^{2+}$	0	>60	—	—	20
,, –CrN_3^{2+}	0	> 1·2	—	—	20

[a] Data are for aqueous solution (various ionic strengths), except for $Co(phen)_3^{2+,3+}$ (aqueous acetone) and ferrocene–ferrocinium (methanol).

[b] This reaction is of uncertain mechanism but is listed here for purposes of comparison.

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[11] Bonner and Hunt, *J. Amer. Chem. Soc.*, 1952, **74**, 1886.

[12] Baker, Basolo, and Neumann, *J. Phys. Chem.*, 1959, **63**, 371.

[13] Lewis, Coryell, and Irvine, *J.*, 1949, 5386.

[14] Stranks, *Discuss. Faraday Soc.*, 1960, **29**, 73.

[15] Zwickel and Taube, (*a*) *Discuss Faraday Soc.*, 1960, **29**, 73; (*b*) *J. Amer. Chem. Soc.*, 1961, **83**, 793; (*c*) *ibid.*, 1959, **81**, 1288.

[16] Sloth and Garner, *J. Amer. Chem. Soc.*, 1955, **77**, 1440.

[17] Deck and Wahl, *ibid.*, 1954, **76**, 4054.

[18] Eichler and Wahl, *ibid.*, 1958, **80**, 4145.

[19] Anderson and Bonner, *ibid.*, 1954, **76**, 3826.

[20] Ball and King, *ibid.*, 1958, **80**, 1091.

[21] Chia and King, *Discuss. Faraday Soc.*, 1960, **29**, 109.

Reaction	Temp.	k_{bi} (l. mole^{-1} sec.$^{-1}$)	$\Delta H\ddagger$ (kcal. mole^{-1})	$\Delta S\ddagger$ (e.u.)	Ref.
Cr^{2+}–$CrNCS^{2+}$	27	$1\cdot8 \times 10^{-4}$	—	—	20
,, –$Cr(NH_3)_5F^{2+}$	25	$2\cdot7 \times 10^{-4}$	13·4	−30	22
,, –$Cr(NH_3)_5Cl^{2+}$	25	$5\cdot1 \times 10^{-2}$	11·1	−23	22
,, –$Cr(NH_3)_5Br^{2+}$	25	0·32	8·5	−33	22
,, –$Cr(NH_3)_5I^{2+}$	25	5·5	—	—	22
,, –$Co(NH_3)_5OH_2{}^{3+}$	20	0·5	2·9	−52	15*c*
,, –$Co(NH_3)_5OH^{2+}$	20	$1\cdot5 \times 10^{6}$	4·6	−18	15*c*
,, –$Co(NH_3)_5Cl^{2+}$	20	$>10^{3}$	—	—	23
,, –$Co(NH_3)_5OAc^{2+}$	25·1	0·18	—	—	24
,, –$Co(NH_3)_5$(H-succinate)$^{2+}$	14·1	0·17	—	—	24
,, –$Co(NH_3)_5$(H-fumarate)$^{2+}$	14·3	0·75	7·5	−33	24
,, –$Co(NH_3)_5$(H-phthalate)$^{2+}$	14·2	0·055	5·1	−47	24
,, –$Co(NH_3)_5$(H-isophthalate)$^{2+}$	14·2	0·11	2·6	−56	24
,, –$Co(NH_3)_5$(H-terephthalate)$^{2+}$	16·6	36	—	—	24
,, –$Co(NH_3)_5$(Me-fumarate)$^{2+}$	2·5	0·43	—	—	24
(c) Reactions of uncertain mechanism					
Fe^{2+}–Fe^{3+}	0	0·87	9·4	−25	25
,, –$FeOH^{2+}$	0	1×10^{3}	6·9	−18	25
,, –FeF^{2+}	0	9·7	8·6	−21	26
,, –$FeF_2{}^{+}$	0	2·5	9·0	−22	26
,, –$FeCl^{2+}$	0	9·7	8·3	−24	25
,, –$FeBr^{2+}$	0	4·9	8·0	25	27
,, –$FeSCN^{2+}$	0	12·2	7·4	−27	29
,, –$FeN_3{}^{2+}$	0	$1\cdot8 \times 10^{3}$	13·2	+6	30
,, –$FeC_2O_4{}^{+}$	0	7×10^{2}	8·6	−14	27
,, –Fe $phen_3{}^{3+}$	25	$3\cdot7 \times 10^{4}$	$\sim$ 0·2	−37	28
V^{2+} –$Co(NH_3)_6{}^{3+}$	25	$3\cdot7 \times 10^{-3}$	9·1	−40	15*b*
,, –$Co(NH_3)_5OH_2{}^{3+}$	25	$\sim$0·5	—	—	15*b*
,, –$Co(NH_3)_5Cl^{2+}$	25	5·7	—	—	15*b*
V^{2+} –V^{3+}	25	$1\cdot0 \times 10^{-2}$	12·6	−25	31
Pu^{3+}–Pu^{4+}	25	20	7·2	−31	32
,, –$PuOH^{3+}$	25	$2\cdot0 \times 10^{4}$	2·2	−32	32
$NpO_2{}^{+}$–$NpO_2{}^{2+}$	4·5	74	11·0	−12	33
V^{3+}–Fe^{3+}	25	5×10^{-3}	16·7	−15	34

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[22] Ogard and Taube, *J. Amer. Chem. Soc.*, 1958, **80**, 1084.

[23] Taube, Myers, and Rich, *ibid.*, 1953, **75**, 4118; Taube and Myers, *ibid.*, 1954, **76**, 2103.

[24] Sebera and Taube, *ibid.*, 1961, **83**, 1785.

[25] Silverman and Dodson, *J. Phys. Chem.*, 1952, **56**, 846.

[26] Hudis and Wahl, *J. Amer. Chem. Soc*, 1953, **75**, 4153.

[27] Horne, Microfilm Diss. Abstr., 1957, **17**, 1673; *J. Phys. Chem.*, 1960, **64**, 1512.

[28] Sutin and Gordon, *J. Amer. Chem. Soc.*, 1961, **83**, 70.

[29] Laurence, *Trans. Faraday Soc.*, 1957, **53**, 1326.

[30] Bunn, Dainton, and Duckworth, *ibid.*, 1959, **55**, 1267.

[31] Krishnamurty and Wahl, *J. Amer. Chem. Soc.*, 1958, **80**, 5921.

[32] Keenan, *J. Phys. Chem.*, 1957, **61**, 1117.

[33] Cohen, Sullivan, and Hindman, *J. Amer. Chem. Soc.*, 1954, **76**, 352; 1957, **79**, 3672.

[34] Higginson, Rosseinsky, Stead, and Sykes, *Discuss. Faraday Soc.*, 1960, **29**, 49.

The first of these criteria is applicable both to inert and to labile complexes. The second is applicable only to reactions in which both metal complexes are substitution-inert but, since it does not depend on a knowledge of the rate-law, it can be employed even when the rate is too fast to be measured. Unfortunately neither criterion is readily applicable to most reactions of aquo-ions, which thus can rarely be proved to be of this type.

The reactions in this class [Table 1(A)] cover a wide range of rates, from $k < 10^{-8}$ l. mole^{-1} sec.$^{-1}$ for the $Co(NH_3)_6{}^{2+}$–$Co(NH_3)_6{}^{3+}$ exchange to $k > 10^5$ for many reactions of the type Fe $phen_3{}^{2+}$–Fe $phen_3{}^{3+}$.[18,10] In general, metal ions surrounded by unsaturated or large polarisable ligands such as *o*-phenthroline, bipyridyl, cyanide, or chloride, exchange electrons rapidly, usually much faster than the corresponding aquo-ions or ammine complexes. The significance of this and of some of the other trends which appear in Table 1 will be considered below.

The demonstration of an outer-sphere mechanism still leaves open the question of how closely the co-ordination shells of the two ions approach each other in the activated complex, particularly with reference to the possibility of intervening solvent or electrolyte layers. Only in a few instances is information about this available. Thus, from the observation that the OH^--catalysed isotopic exchange between $Co(NH_3)_n{}^{2+}$ and $Co(NH_3)_6{}^{3+}$ (corresponding to the rate law, $k[Co(NH_3)_n{}^{2+}]\ [Co(NH_3)_6{}^{3+}\cdot OH^-]$) is accompanied by OH^- substitution on the newly created Co^{III} ion, Stranks[14] concludes that electron transfer occurs predominantly through the intermediate

$$[(NH_3)_5Co^{III}\cdot NH_3\cdot OH\cdot Co^{II}(NH_3)_n]$$

rather than through

$$[(NH_3)_5Co^{III}\cdot NH_3\cdot OH\cdot NH_3Co^{II}(NH_3)_{n-1}].$$

It seems reasonable that the Cl^--catalysed exchange proceeds through an analogous intermediate $[(NH_3)_5Co^{III}\cdot NH_3\cdot Cl\cdot Co^{II}(NH_3)_n]$, but in this case the rapid hydrolysis of the Co^{III} chloroammine precludes demonstration of net Cl^- transfer. The markedly Cl^--catalysed oxidation of Cr^{2+} by $Co(NH_3)_6{}^{3+}$, which yields $CrCl^{2+}$, presumably proceeds through a similar intermediate.[35]

The rates of certain outer-sphere reactions exhibit marked sensitivity to ions of opposite sign, *e.g.*, the $MnO_4{}^{2-}$–$MnO_4{}^-$ exchange[1] which is accelerated by cations in the order $Cs^+ > K^+$, $Na^+ > Li^+$. This may be due simply to salt effects or, alternatively, to the operation of electron transfer paths involving outer-sphere bridged intermediates such as, $[O_3MnO–Cs–OMnO_3]^{2-}$.

Closely related to the reactions of metal complexes in this class, in that they involve electron transfer between extensively delocalised orbitals with little accompanying structural rearrangement, are certain electron-

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[35] Taube, *Chem. Soc. Special Publ.*, No. 13, 1959, p. 57.

transfer reactions between organic molecules and anions (*e.g.*, naphthalene and its mononegative ion) whose rates have been measured by electron spin resonance spectroscopy.[4] For the exchange between naphthalene and its anion in tetrahydrofuran a cation-bridged intermediate, having a sandwich structure with a solvated cation (*e.g.*, Na^+) lying between the two hydrocarbon systems, has been proposed.[36] Since the anion and the cation are strongly associated in this medium it is to be expected that electron transfer will be accompanied by transfer of the cation to the newly formed anion, and will thus appear as a net atom transfer. Electron spin resonance measurements yield direct evidence for this in the case of electron transfer to benzophenone from its sodium ketyl.[4b]

Inner-sphere Reactions.—In reactions of this class, which have been studied particularly by Taube and his co-workers, electron transfer is preceded by substitution into the co-ordination shell of one of the ions, with the formation of a bridged intermediate in which the two metal ions are linked by a common ligand. A typical reaction of this type is:

$$\mathrm{Cr^{2+} + (NH_3)_5Co^{III}X + 5H^+ \rightarrow Cr^{III}X + Co^{II} + 5NH_4^+} \quad . \; . \; . \; . \; . \quad (6)$$

where X may be any of a large number of molecules or anions, *e.g.*, H_2O, OH^-, Cl^-, OAc^-, etc. [Table 1(B)]. In each case it is found that X appears in the co-ordination shell of the newly formed Cr^{III} ion. (In the cases of H_2O and OH^-, oxygen transfer has been demonstrated by ^{18}O labelling of the oxidant.[37]) Since both the Co^{III} complex and the Cr^{III} product are substitution-inert, this implies that electron transfer occurs through the bridged intermediate (I) which is formed by an initial substitutional step:

$$\mathrm{(NH_3)_5Co^{III}X + Cr(H_2O)_6^{2+} \rightarrow \underset{(I)}{[(NH_3)_5Co^{III}\text{–}X\text{–}Cr^{II}(H_2O)_5]} + H_2O} \quad . \quad (7)$$

Similar mechanisms have been demonstrated for electron transfer between Cr^{2+} and various chromic complexes[21,22] of the type $(H_2O)_5Cr^{III}X$ and $(NH_3)_5Cr^{III}X$; also for various Pt^{II}–Pt^{IV} exchange reactions, for example,[38] $Pt\,en_2^{2+}$–$Pt\,en_2Cl_2^{2+}$. The last reaction and its analogues are catalysed by Cl^- according to the rate-law, $k[Pt\,en_2^{2+}][Pt\,en_2Cl_2^{2+}][Cl^-]$, suggesting that electron transfer occurs through the symmetrical bridged intermediate (II).

$$\mathrm{{}^*Cl^- + Pt\,en_2^{2+} + Pt\,en_2Cl_2^{2+} \rightarrow}$$
$$\mathrm{\underset{(II)}{[{}^*Cl\text{–}Pt\,en_2\text{–}Cl\;\;Pt\,en_2\text{–}Cl]^{3+}} \rightarrow Pt\,en_2{}^*Cl_2^{2+} + Pt\,en_2^{2+} + Cl^-} \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

The accompanying exchange with isotopically labelled Cl^- in the solution (which may be used to follow the reaction, $Pt\,en_2Cl_2^{2+}$ being substitution-inert) confirms the mechanism.

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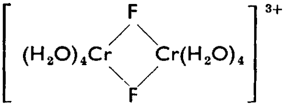
[36] Aten, Dieleman, and Hoijtink, *Discuss. Faraday Soc.*, 1960, **29**, 182.
[37] Kruse and Taube, *J. Amer. Chem. Soc.*, 1960, **82**, 526.
[38] Basolo, Morris, and Pearson, *Discuss. Faraday Soc.*, 1960, **29**, 80.

In all these reactions the bridged intermediate, following electron transfer, contains one labile bond (*e.g.*, Co^{II}–X or Pt^{II}–X) and is thus decomposed too rapidly to be detected. In one case, however, the oxidation of $Co(CN)_5^{3-}$ by $Fe(CN)_6^{3-}$, where both metal ligand bonds are substitution-inert, a product believed to have the bridged structure $[(NC)_5Co^{III}\cdot NC\cdot Fe^{II}(CN)_5]^{6-}$ has actually been isolated.[39]

Although inner-sphere bridged mechanisms of this type are probably fairly common, they can be demonstrated unequivocally only in certain cases, the minimum requirement being that the reactant complex of one of the metal ions and the product complex of the other be substitution-inert. Unfortunately this condition, like that for the demonstration of the outer-sphere mechanism, is rarely fulfilled for reactions between aquo-ions.

The observation of catalysis by anions, even when accompanied by their incorporation into the co-ordination shell of one of the products, does not necessarily reflect the participation of the anion as a bridging ligand. Thus SO_4^{2-} and $P_2O_7^{4-}$ accelerate the oxidation of Cr^{2+} by $(NH_3)_5CoOH_2^{3+}$ and each is incorporated into the product Cr^{III} complex.[40] Similarly, during the oxidation of Cr^{2+} by $(NH_3)_5CoCl^{2+}$ in the presence of $P_2O_7^{4-}$, both Cl^- and $P_2O_7^{4-}$ are incorporated into the product Cr^{III} complex. The structure of the activated complex in these cases (where X is the bridging and Y the non-bridging anion) presumably is $(NH_3)_5Co^{III}$–X–$Cr^{II}(H_2O)_4Y$. Not unexpectedly, it is found that the catalytic effect of anions as non-bridging ligands is much smaller than as bridging ligands.

Although the possibility of doubly bridged intermediates, with structures analogous, for example, to that of Al_2Cl_6, has been considered in certain reactions,[41] there is no direct evidence for them. Chia and King[21] have shown that electron transfer between Cr^{2+} and *cis*-CrF_2^+ proceeds predominantly through the singly bridged intermediate $[(H_2O)_4F–Cr–F–Cr(H_2O)_5]^{3+}$ rather than the symmetrical species



Similarly, apparently only one oxygen is involved[37] in bridging (and is transferred) in the oxidation of Cr^{2+} by *cis*-$(NH_3)_4Co(H_2O)_2^{3+}$ or *cis*-en_2 $Co(H_2O)_2^{3+}$.

Although the transfer of the bridging ligand from the oxidant to reductant constitutes the evidence for the bridged mechanism in the cases cited it is not clear that such a transfer is an essential feature of this mechanism

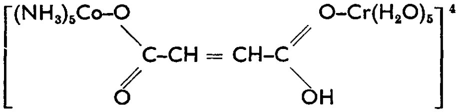
[39] Hain and Wilmarth, *J. Amer. Chem. Soc.*, 1961, **83**, 509.

[40] Taube, *ibid.*, 1955, **77**, 4481.

[41] Carpenter, Ford-Smith, Bell, and Dodson, *Discuss. Faraday Soc.*, 1960, **29**, 92.

since in these instances it follows simply from a consideration of the relative substitution-lability of the two metal–ligand bonds after electron transfer. The oxidation of Cr^{2+} by $IrCl_6^{2-}$ is also believed[23] to proceed through a Cl^--bridged mechanism, but in this case the products are $IrCl_6^{3-}$ and $Cr(H_2O)_6^{3+}$. The description of inner-sphere mechanisms as atom transfer[42] (as distinct from electron transfer) processes may thus be somewhat misleading. This point also is emphasised by the Cl^--bridged Pt^{II}–Pt^{IV} exchanges (equation 8) which involve the transfer of two electrons and thus are *not* equivalent simply to the transfer of a Cl atom from Pt^{IV} to Pt^{II} (Cl^+ transfer seems an even less realistic concept). Possibly a more meaningful distinction between concepts of electron and atom (or group) transfer in the present context could be made in terms of the actual mechanism of the electron-transfer process, the former being used to denote "conduction" mechanisms which do not involve actual oxidation or reduction of the bridging group, and the latter "chemical" mechanisms in which an electron is transferred by a process of successive oxidation and reduction of the ligand (or *vice versa*) by the two metal ions. The two mechanisms are, at least in principle, quite distinguishable.[43]

Not surprisingly, the rates of inner-sphere redox reactions are very sensitive to the nature of the bridging group, reflecting the essential role of the latter in the electron-transfer process. Thus the data in Table 1 reveal a 10^6-fold variation in the rate of oxidation of Cr^{2+} by $Co^{III}(NH_3)_5X$ when the bridging ligand X is varied. The high rates for terephthal and fumarate, relative to the other carboxylic acids in this series, are of special interest and have been interpreted in terms of bridged intermediates such as



in which the two metal ions are co-ordinated to different carboxyl groups, the electron being transferred between them by "conduction" through the conjugated π-electron system. Strong support for this is provided by the observation that in the corresponding oxidation of Cr^{2+} by $(NH_3)_5Co^{III}{\cdot}O{\cdot}OC{\cdot}CH{:}CH{\cdot}CO{\cdot}OMe$, electron transfer is accompanied by hydrolysis of the ester and incorporation of the methyl alcohol into the co-ordination shell of the Cr^{III} product. With hydrogen maleate or methyl maleate (but not the corresponding fumarates) as the bridging ligand, and Cr^{2+} or V^{2+} as reductant, *cis-trans*-isomerisation and hydrogen exchange with the solvent (D_2O) also accompany electron transfer, and this has been construed as evidence that an electron passes into the maleate group during the reaction.[44]

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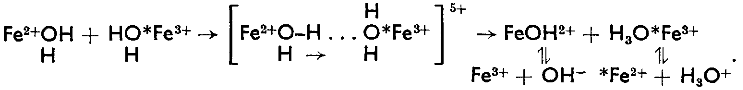
[42] Stewart, *Experientia*, 1959, **15**, 401.

[43] Halpern and Orgel, *Discuss. Faraday Soc.*, 1960, **29**, 92.

[44] Fraser, Sebera, and Taube, *J. Amer. Chem. Soc.*, 1959, **81**, 1906; Fraser and Taube, *ibid.*, 1959, **81**, 5000, 5514; *ibid.*, 1961, in press.

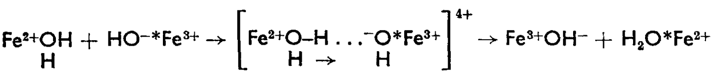
Electron transfer between Cr^{2+} and CrN_3^{2+}, which is accompanied by transfer of N_3^-, is also believed to proceed through a polyatomic bridge ($Cr\text{–}N{=}N{=}N\text{–}Cr$); the much lower rate observed with $CrNCS^{2+}$ is attributed to the unsymmetrical structure of the corresponding NCS^--bridged intermediate, in which electron transfer leads to the formation of an unstable $CrSCN^{2+}$ complex.[20] The possibilities afforded by the use of such conjugated bridging groups for elucidating details of the electron-transfer mechanism and for systematic variation of structural and electronic parameters make these systems extremely valuable, and their study promises to play an important role in the further development of the subject.

Hydrogen Transfer and Bridging Mechanisms (D_2O Isotope Effects).—A possible mechanism of electron transfer between metal aquo-ions, first suggested by Dodson and Davidson,[45] is through transfer of a hydrogen atom between the hydration shells. For the $Fe^{2+}\text{–}Fe^{3+}$ reaction this path may be depicted as:



$$\mathrm{Fe^{2+}\underset{H}{O}H + H\underset{H}{O}{}^{*}Fe^{3+} \rightarrow \left[Fe^{2+}O\text{–}\underset{H\,\rightarrow}{H} \ldots \overset{H}{\underset{H}{O}}{}^{*}Fe^{3+} \right]^{5+} \rightarrow \begin{array}{c} FeOH^{2+} \\ \upharpoonleft\!\downharpoonright \\ Fe^{3+} + OH^{-} \end{array} + \begin{array}{c} H_3O^{*}Fe^{3+} \\ \upharpoonleft\!\downharpoonright \\ {}^{*}Fe^{2+} + H_3O^{+} \end{array}} \quad . \quad . \quad (9)$$

or, for the $Fe^{2+}\text{–}FeOH^{2+}$ exchange:



$$\mathrm{Fe^{2+}\underset{H}{O}H + HO^{-}{}^{*}Fe^{3+} \rightarrow \left[Fe^{2+}O\text{–}\underset{H\,\rightarrow}{H} \ldots {}^{-}\underset{H}{O}{}^{*}Fe^{3+} \right]^{4+} \rightarrow Fe^{3+}OH^{-} + H_2O^{*}Fe^{2+}} \quad . \quad (10)$$

the intermediate in the latter case being symmetrical. Among the evidence which has been advanced in support of such a mechanism is the following:

(1) The activation energies of a surprisingly large number of diverse redox reactions involving metal aquo-ions are close to 10 kcal./mole, and their activation entropies close to —25 e.u., suggesting that they proceed by a common mechanism which probably involves water.[46]

(2) In certain redox reactions involving metal complexes there seems to be a requirement that at least one of the inner shell ligands be a water molecule,[46] *e.g.*, one of the CN^- ions must be replaced by a water molecule before $Fe(CN)_6^{4-}$ is oxidised by hydroperoxide. Similarly, the electrolytic reduction of $Cd(CN)_4^{2-}$ proceeds through the aquotricyano-complex.

(3) The rates of the $Fe^{2+}\text{–}Fe^{3+}$ and the $Fe^{2+}\text{–}FeOH^{2+}$ reaction are lowered by a factor of 2 in passing from H_2O to D_2O as solvent.[47] While this isotope effect is consistent with a mechanism involving breaking of an O–H bond, the support it provides for it is not compelling in view of uncertainties concerning the differences in solvent characteristics of H_2O and D_2O and of the D_2O isotope effects observed in other redox reactions (Table 2). Thus even larger deuterium isotope effects are found in the

[45] Dodson and Davidson, *J. Phys. Chem.*, 1952, **56**, 866.

[46] Reynolds and Lumry, *J. Chem. Phys.*, 1955, **23**, 2460.

[47] (*a*) Hudis and Dodson, *J. Amer. Chem. Soc.*, 1956, **78**, 911; (*b*) Sutin and Dodson, personal communication.

TABLE 2. D_2O *Isotope effects in redox reactions.*

Reaction	k_{H_2O}/k_{D_2O}	Ref.
Fe^{2+}–Fe^{3+}	2	47*a*
Fe^{2+}–$FeOH^{2+}$	2	47*a*
Fe^{2+}–$FeCl^{2+}$	2·5	47*b*
Fe^{2+}–FeN_3^{2+}	1·5	30
NpO_2^+–NpO_2^{2+}	1·4	33
Cr^{2+}–$Co(NH_3)_6^{3+}$	1·3	15*b*
Cr^{2+}–$Co(NH_3)_5OH_2^{3+}$	3·8	15*c*
Cr^{2+}–$Co(NH_3)_5OH^{2+}$	2·6	15*c*
Cr^{2+}–$Co(NH_3)_5Cl^{2+}$	1·3	22
Cr^{2+}–$Co(NH_3)_5$ (H-fumarate)	$\sim$1	24
$Cr(dipy)_3^{2+}$–$Co(NH_3)_6^{3+}$	1·0[a]	15*a*
$Cr(dipy)_3^{2+}$–$Co(NH_3)_5OH_2^{3+}$	2·6	15*a*
Tl^+–Tl^{3+}	$\sim$1·5	48
Co^{2+}–Co^{3+}	2	11
V^{2+}–$Co(NH_3)_6^{3+}$	1·7	15*b*
V^{2+}–$Co(NH_3)_5Cl^{2+}$	2·2	15*b*

[a] There is, however, a 30% reduction in the rate of this reaction in going from $Co(NH_3)_6^{3+}$ to $Co(ND_3)_6^{3+}$ as oxidant;[15] this is probably related in origin to some of the D_2O isotope effects for aquo-ions.

oxidations of Cr^{2+} by $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5OH^{2+}$ which are known[37] to proceed through inner-sphere oxygen-bridged mechanisms and in the oxidation of Cr $dipy_3^{2+}$ by $Co(NH_3)_5OH^{2+}$. The latter reaction presumably proceeds by an outer-sphere mechanism but in this case water is absent from the co-ordination shell of the reductant. An appreciable, although somewhat smaller, D_2O isotope effect is observed even for electron transfer between Cr^{2+} and $Cr(NH_3)_5Cl^{2+}$ which is known to proceed by a Cl^--bridged mechanism.*

On energetic grounds there are some objections to the suggestion of a net hydrogen transfer in a reaction such as (9). The endothermicity of this process is expected to approach that of the self-ionisation of water ($\sim$13 kcal./mole) and this is difficult to reconcile with an observed activation energy of 10 kcal./mole.

A somewhat modified view[10,27] of the role of water in these reactions, which probably has greater validity, is that coupling of the hydration shells of the two ions by hydrogen bonding lowers the energy of the activated complex and, by increasing the overlap between the exchanging orbitals, provides a more effective conducting path for electron transfer. In this context, transfer of hydrogen (as with other bridging groups) is incidental to its bridging role, and whether or not it occurs depends on the relative proton affinities of the two hydration shells after electron transfer. Thus hydrogen transfer would be expected to accompany reaction (10) but not (9).

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*Other studies of kinetic isotope effects in redox reactions might also be mentioned in this context. Murmann, Taube, and Pausey[49] found an appreciable oxygen isotope effect [$k(^{16}O)/k(^{18}O) = 1{\cdot}035$] in the inner-sphere oxidation of Cr^{2+} by $Co(NH_3)_5OH_2^{3+}$, suggesting appreciable weakening of the Co—O bond in the oxygen-bridged activated complex. This reaction also exhibits a smaller, but measurable, nitrogen isotope effect [$k(^{14}N)/k(^{15}N) = 1{\cdot}003$] indicative of some weakening of the Co—N bonds.

[48] Gilks and Waind, *Discuss. Faraday Soc.*, 1960, **29**, 102.

[49] Murmann, Taube, and Pausey, *J. Amer. Chem. Soc.*, 1957, **79**, 262.

Reactions of Uncertain Mechanism.—The uncertainties concerning the detailed mechanism of the Fe^{2+}–Fe^{3+} exchange extend also to the redox reactions of most other aquo-ions and labile complexes. For these reactions the conditions required for unequivocal demonstration of either the outer- or inner-sphere mechanism are generally not fulfilled and, at least at this stage, their mechanisms must be inferred indirectly. Only very limited progress has been made in this direction and it is in this area that some of the most important and challenging problems connected with the study of electron-transfer mechanisms are at present to be found.

Attempts so far to infer the mechanisms of such reactions have invoked some of the following criteria.

(1) *Comparisons with reactions of known mechanism.* Such comparisons involve particularly the study of ligand effects. The special role of the bridging ligand in the inner-sphere mechanism might be expected to give rise to a different pattern of dependence of the rate on the nature of the ligand from that observed for outer-sphere reactions, thus providing a diagnostic tool for distinguishing between the two types. Thus, the observation that the relative rates of oxidation of V^{2+} by the series of Co^{III} complexes, $Co(NH_3)_6{}^{3+}$, $Co(NH_3)_5OH_2{}^{3+}$, $Co(NH_3)_5OH^{2+}$, and $Co(NH_3)_5Cl^{2+}$, (Table 3) parallels more closely the relative rates of oxidation of $Cr(bipy)_3{}^{2+}$ than of Cr^{2+} has led Zwickel and Taube[15b] to conclude that the oxidation of V^{2+} in these cases, unlike that of Cr^{2+}, involves an outer-sphere mechanism. Similary it would appear, although contrary arguments also have been advanced[9] that the small dependence of the rate of Fe^{2+}–FeX^{2+} exchange (Table 1) on the identity of the halide X^-, compared with the large variations found in the Cr^{2+}–CrX^{2+} and Cr^{2+}–$Co(NH_3)_5X^{2+}$ reactions, argues against an inner-sphere bridging role for the halide in the case of Fe^{2+}–FeX^{2+}; also the 10^3-fold difference between the Fe^{2+}–Fe^{3+} and Fe^{2+}–$FeOH^{2+}$ rates is considerably smaller than the corresponding difference between the inner-sphere Cr^{2+}–$Co(NH_3)_5OH_2{}^{3+}$ and Cr^{2+}–$Co(NH_3)_5OH^{2+}$ reactions, but does not appear unreasonable for an outer-sphere hydrogen-bridged mechanism. In this connexion it is of interest that in the outer-sphere oxidation of $Cr\,dipy_3{}^{2+}$ where, owing to the absence of water from the co-ordination shell of the reductant, hydrogen bridging of this type is not possible, the rate for $Co(NH_3)_5OH^{2+}$ as oxidant is actually slightly lower than for $Co(NH_3)_5OH_2{}^{3+}$.[15] On the other hand, the large effect of $N_3{}^-$ on the Fe^{2+}–Fe^{3+} exchange and the somewhat different $\Delta H\ddagger$ and $\Delta S\ddagger$ values for the Fe^{2+}–$FeN_3{}^{2+}$ reaction, are suggestive[50] of a different mechanism in this case, possibly an inner-sphere mechanism similar to that for Cr^{2+}–$CrN_3{}^{2+}$.[20] Unfortunately the patterns of ligand effects for the few reactions of known mechanism so far studied are not sufficiently distinctive or well understood for conclusions such as these to be drawn with great confidence. The accumulation of more results of this type for reactions of

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[50] Dainton, *Discuss. Faraday Soc.*, 1960, **29**, 125.

TABLE 3. *Relative* rates of oxidation of* V^{II} *and* Cr^{II} *by various* Co^{III} *complexes (after Zwickel and Taube*[15b]*).*

Oxidant	Reductant		
	$Cr^{2+}aq$	$V^{2+}aq$	Cr $dipy_3^{2+}$
$Co(NH_3)_6^{3+}$	1	1	1
$Co(NH_3)_5OH_2^{3+}$	6×10^3	135	91
$Co(NH_3)_5OH^{2+}$	2×10^{10}	10^7	50
$Co(NH_3)_5Cl^{2+}$	10^5	$1{\cdot}6 \times 10^3$	$1{\cdot}5 \times 10^3$

*Relative to $Co(NH_3)_{66}^+$ in each case.

known mechanism, however, will undoubtedly enhance the value of this approach.

In a few cases the mechanistic inferences to be drawn from the study of ligand effects seem more convincing. For example, the hydrolysis of the bridging ester which accompanies the inner-sphere oxidation of Cr^{2+} (but not the outer-sphere oxidation of Cr $dipy_3^{2+}$) by $(NH_3)_5Co^{III}$(Me fumarate) is also observed with V^{2+} as reductant, strongly implying an inner-sphere mechanism also for the latter reaction.[35,44]

(2) *$\Delta S\ddagger$ and related kinetic parameters.* The measurement of kinetic parameters, particularly of $\Delta S\ddagger$ which is related to the structure of the activated complex, might also be expected to provide information about the mechanism of electron-transfer reactions. Although some attempts in this direction have been made,[51] the relatively few results now available (Table 1) for reactions of known mechanism do not appear to yield sufficiently distinctive patterns for the mechanism of, say, the Fe^{2+}–Fe^{3+} exchange, to be assigned with confidence on this basis. The potential usefulness of the method thus rests on the accumulation of more extensive and more accurate data and on the achievement of a better understanding of the influence on $\Delta S\ddagger$ of other specific factors, notably the charges of the reacting ions, the ionic strength, and (in the case of reactions involving a net chemical change) of the overall entropy of reaction.

The dependence of $\Delta S\ddagger$ on the charges of the reacting ions has been discussed by several authors.[52,34] Newton and Rabideau[52] showed that for a large number of redox reactions of the actinide elements (including simple electron transfers and reactions involving hydrolytic changes) the *entropy* of the activated complex, $S\ddagger$ (given by $S\ddagger = \Delta S\ddagger + \Sigma S^\circ_{\text{reactant}}$) is largely a function of its charge. For activated complexes of charge $+3$, $+4$, $+5$, and $+6$, values of $S\ddagger$ (presumably reflecting largely the hydration of the activated complex) were found to lie in the ranges 29—40, 67—81, 72—106, and 102—128 e.u., respectively. Higginson *et al.*,[34] on the other hand, have drawn attention to a correlation (shown graphically in Fig. 1) between $-\Delta S\ddagger$ and the charge of the activated complex for a number of isotopic exchange reactions, and to the fact that many electron-transfer reactions involving a net chemical change exhibit deviations from

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[51] Higginson, *Discuss. Faraday Soc.*, 1960, **29**, 123.
[52] Newton and Rabideau, *J. Phys. Chem.*, 1959, **63**, 365.

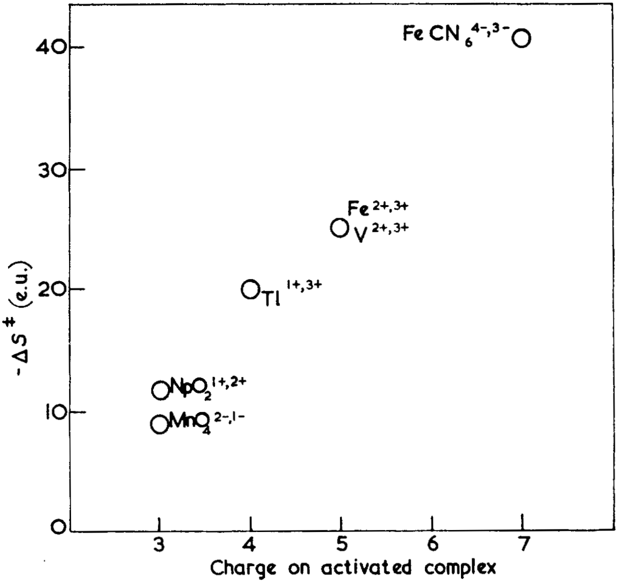

FIG. 1. *Dependence of $\Delta S^{\ddagger}$ of isotopic exchange reactions on the charge of the activated complex* (based on the data cited by Higginson *et al.*[34]).

this correlation in the direction of the entropy of reaction, ΔS° (*e.g.*, Tl^{+}–Co^{3+}, $\Delta S^{\ddagger} = +5$, $\Delta S^{\circ} = +30$; Ag^{+}–Ce^{4+}, $\Delta S^{\ddagger} = +2$, $\Delta S^{\circ} = +20$; Fe^{2+}–Tl^{3+}, $\Delta S^{\ddagger} = -5$, $\Delta S^{\circ} = +10$). When fitted to a relation of the type (where $\Delta S^{\ddagger}_{(0)}$ is the entropy of activation, based on the correlation in Fig. 1, expected for a reaction with $\Delta S^{\circ} = 0$),

$$(\Delta S^{\ddagger} - \Delta S^{\ddagger}_{(0)}) = \alpha \Delta S^{\circ} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

values of α for these reactions were found to range from 0·5 to 1, *i.e.*, the additional contribution to the entropy of activation corresponds to a large fraction of overall entropy of reaction. Since the entropy of reaction arises largely from changes in the hydration of the ions, this implies that the configuration of the activated complex approaches rather closely to that of the final product; this is more readily reconciled with an "extended" (*i.e.*, outer-sphere) than with a "compact" structure for the activated complex for the reactions in question. Such interpretations are clearly subject to considerable uncertainty but serve to illustrate the possibilities of this approach.

For electron-transfer reactions where there are accompanying hydrolytic changes, *e.g.*, $Co^{3+} + V^{3+} + H_2O \rightarrow Co^{2+} + VO^{2+} + 2H^{+}$, analogous entropy correlations suggest that at least partial hydrolysis occurs in the activated complex.[34]

Taube[9] has drawn attention to differences in $\Delta S^{\ddagger}$ between certain bridged electron-transfer reactions and related non-redox reactions which proceed through structurally similar activated complexes, *e.g.*, $(NH_3)_5CrBr^{2+} + Cr^{2+}$, $\Delta S\ddagger = -33$ e.u.; $(NH_3)_5CrBr^{2+} + Hg^{2+}$, $\Delta S\ddagger = -16$ e.u. The difference was attributed to more stringent requirements in the way of simultaneous bond rearrangement in the case of the electron-transfer reaction.

A relation between $\Delta H\ddagger$ and the heat of reaction ΔH°, paralleling that noted above for entropies, was found by Newton and Rabideau[52] to hold for a large number of redox reactions of the actinide elements. Within this correlation, $\Delta H\ddagger$ for purely "electron-transfer" reactions (*e.g.*, $Pu^{3+} + PuO_2^{2+} \rightarrow Pu^{4+} + PuO_2^{+}$) appeared to be somewhat lower than for reactions involving hydrolytic or structural changes (*e.g.*, $Np^{4+} + NpO_2^{2+} + 2H_2O \rightarrow 2NpO_2^{+} + 4H^{+}$), presumably reflecting an additional contribution to $\Delta H\ddagger$ from bond rearrangement in the latter cases.

Another kinetic parameter which is potentially capable of providing information about the structure of the activated complex and helping to distinguish between inner- and outer-sphere mechanisms, is the volume of activation $\Delta V\ddagger$ determined from the pressure-dependence of the rate. Measurements of this type have not as yet been reported on electron-transfer reactions, but a recent study of the mechanism of a substitution reaction[53] serves to illustrate their possible value.

(3) *Solvent effects.* One of the chief uncertainties in the mechanisms of electron-transfer reactions relates to the participation of the solvent (*e.g.*, in the case of aquo-ions to the number of co-ordinated water molecules in the activated complex). One approach to gaining more information about this is through the study of solvent effects. The study of redox reactions in D_2O has been vigorously pursued from this standpoint but in relatively few instances has the study of redox reactions between metal ions been extended to non-aqueous solvents. The Fe^{II}–Fe^{III} exchange has been examined for reaction in nitromethane[54a] and in various alcohols[28] and found in all these cases to be much slower than in water; in alcohol the reaction is markedly accelerated, according to a first-order rate law, by small amounts of water, supporting the view that the latter plays a specific role in the mechanism. Other redox studies in non-aqueous media include those on the Ce^{III}–Pb^{IV} and Co^{II}–Pb^{IV} reactions in acetic acid[55] and the U^{IV}–U^{VI} exchange reaction in methanol–water mixed solvents.[56] The latter reaction exhibits marked changes in kinetics, and apparently in mechanism, with solvent composition. In all these cases interpretation of the results and inferences concerning details of mechanism are severely limited by an insufficient understanding of the properties of ionic species in non-aqueous solvents. Considerably more experience with systems of this type will be required before they can be interpreted with confidence.

[53] Hunt and Taube, *J. Amer. Chem. Soc.*, 1958, **80**, 2642.

[54] (*a*) Maddock, *Trans, Faraday Soc.*, 1959, **55**, 1268; (*b*) Sutin, *J. Phys. Chem.*, 1960, **64**, 7766.

[55] Benson and Sutcliffe, *Trans. Faraday Soc.*, 1960, **56**, 246; Benson, Proll, Sutcliffe, and Walkley, *Discuss. Faraday Soc.*, 1960, **29**, 60.

[56] Mathews, Hefley, and Amis, *J. Phys. Chem.*, 1959, **63**, 1236.

Two-equivalent Redox Reactions

The transition metals normally exhibit stable oxidation states differing by one electron and react with each other by 1-equivalent steps. On the other hand, the stable oxidation states of the post-transition elements usually differ by two electrons (*e.g.*, $\mathrm{Sn^{II}}$–$\mathrm{Sn^{IV}}$; $\mathrm{Tl^{I}}$–$\mathrm{Tl^{III}}$; $\mathrm{Hg_2^{2+}}$ –$\mathrm{2Hg^{II}}$). The question thus arises whether reactions involving these redox couples [*e.g.*, (2) and (3)] occur in a single step or by successive 1-equivalent steps. In considering this it is convenient to discuss first non-complementary reactions (2-equivalent oxidant + 1-equivalent reductant or *vice versa*) and then complementary ones (2-equivalent oxidant + 2-equivalent reductant).

Non-complementary reactions.—The simple mechanisms which might be expected to operate in non-complementary redox reactions, a typical one involving, say, the oxidation of A^+ to A^{2+} and the reduction of B^{2+} to B, are of four types:

I. One-step termolecular mechanism.

$$2A^+ + B^{2+} \rightarrow 2A^{2+} + B$$

II. Bimolecular mechanism: initial 1-equivalent step.

$$\begin{aligned} A^+ + B^{2+} &\rightarrow A^{2+} + B^+ \\ A^+ + B^+ &\rightarrow A^{2+} + B \end{aligned}$$

III. Bimolecular mechanism: initial 2-equivalent step.

$$\begin{aligned} A^+ + B^{2+} &\rightarrow A^{3+} + B \\ A^+ + A^{3+} &\rightarrow 2A^{2+} \end{aligned}$$

IV. Bimolecular mechanism: initial disproportionation.

$$\begin{aligned} 2A^+ &\rightarrow A + A^{2+} \\ A + B^{2+} &\rightarrow A^{2+} + B \end{aligned}$$

In each of the last three cases the earlier step, which involves the formation of an unstable species, would presumably be the slower.

Shaffer's principle of equi-valency change[57,58] which notes that non-complementary reactions are often slower than similar complementary ones (*e.g.*, the slow reduction of $\mathrm{Tl^{III}}$ by $\mathrm{Fe^{II}}$ or of $\mathrm{Ce^{IV}}$ by $\mathrm{Tl^{I}}$ compared with the rapid reduction of $\mathrm{Tl^{III}}$ by $\mathrm{Sn^{II}}$ and of $\mathrm{Ce^{IV}}$ by $\mathrm{Fe^{II}}$) finds rationalisation in terms of this picture. Thus the first of the above mechanisms is expected to be slow because it involves a termolecular step, and the other three because they involve the formation of unstable intermediates (B^+, A^{3+}, and A, respectively). Not unexpectedly, however, because of the other specific factors which influence the rates of redox reactions and because of the possibilities for stabilisation of intermediate oxidation states, the equi-valency principle has only limited validity and many apparent exceptions are to be found.[58]

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[57] Shaffer, *J. Amer. Chem. Soc.*, 1933, **55**, 2169; *J. Phys. Chem.*, 1936, **40**, 1021; *Cold Spring Harbor Symp. Quant. Biol.*, 1939, **1**, 50.

[58] Halpern, *Canad. J. Chem.*, 1959, **37**, 148.

There is evidence that at least the first three of the above mechanisms occur. The termolecular mechanism (type I), corresponding to the rate-law $k[A^+]^2[B^{2+}]$, is readily distinguished kinetically from the others and several cases involving the oxidation or reduction of metal ions by oxygen and hydrogen, respectively (*e.g.*, 2 $Fe^{II} + O_2$;[59] $2Pu^{III} + O_2$;[60] $2Ag^+ + H_2$[61]) have been observed. However, with the possible exception of one of the paths in the oxidation of Co^{II} by Pb^{IV} in acetic acid[55] there is no known instance of a reaction involving three metal ions which proceeds by this mechanism.

In the limiting case both type II and type III mechanisms yield bimolecular rate-laws, $k[A^+][B^{2+}]$, and a kinetic distinction between them becomes possible only in the favourable case where reversal of the first step is fast enough to compete with the second one, for then inhibition by one or other of the products is observed. An example where an initial 1-electron step has been demonstrated[62] is the reaction, $2Fe^{II} + Tl^{III} \rightarrow 2Fe^{III} + Tl^{I}$, which is inhibited by Fe^{III} according to the rate-law, $k_1k_2[Fe^{II}]^2[Tl^{III}]/(k_{-1}[Fe^{III}] + k_2[Fe^{II}])$ which fits the mechanism

$$Fe^{II} + Tl^{III} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe^{III} + Tl^{II} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

$$Fe^{II} + Tl^{II} \xrightarrow{k_2} Fe^{III} + Tl^{I} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

Similar mechanisms have been demonstrated for $2Co^{III} + Tl^{I}$,[63] and for $2V^{IV} + Tl^{III}$,[34] and are considered likely for many other reactions on the basis of the relative plausibilities of the two alternative intermediates; for example, U^{V} is considered more likely than Fe^{I} as an intermediate in the reaction $U^{IV} + 2Fe^{III} \rightarrow U^{VI} + 2Fe^{II}$.[64] On the other hand, inhibition by Pb^{II} suggests that one of the paths in the oxidation of Co^{II} by Pb^{IV} in acetic acid involves an initial 2-equivalent step with the formation of Co^{IV} as intermediate.[55]

Mechanisms of type IV are rare. They might be expected to operate in cases where the species A and A^{3+} are both known to have considerable stability, *e.g.*, in the reaction $2V^{IV} + Tl^{III} \rightarrow 2V^{V} + Tl^{I}$. The kinetics of this reaction,[34] however, point to a type II mechanism with, at most, minor contributions from the alternative path involving disproportionation of V^{IV}. One instance of electron transfer which apparently proceeds by a disproportionation mechanism is the Ag^{I}–Ag^{II} isotopic exchange.[65] The observed rate-law in this case, $k[Ag^{II}]^2$, is consistent with the disproportionation $2Ag^{II} \rightleftharpoons Ag^{I} + Ag^{III}$ as the principal exchange path and leads to the surprising conclusion that the rate constant for this step ($1{\cdot}0 \times 10^{3}$ l. $mole^{-1}$

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[59] George, *J.*, 1954, 4349.
[60] Baker and Newton, *J. Phys. Chem.*, 1957, **61**, 381.
[61] Webster and Halpern, *ibid.*, 1957, **61**, 1239.
[62] Ashurst and Higginson, *J.*, 1953, 3044.
[63] Ashurst and Higginson, *ibid.*, 1956, 343.
[64] Betts, *Canad. J. Chem.*, 1955, **33**, 1780.
[65] Gordon and Wahl, *J. Amer. Chem. Soc.*, 1958, **80**, 273.

sec.$^{-1}$ at 0°) is at least 100 times that for direct electron transfer between Ag^{I} and Ag^{II}. It is also appropriate to mention in this context the reaction, $Hg_2^{2+} + Tl^{III} \rightarrow 2Hg^{II} + Tl^{I}$, whose kinetics, $k[Hg_2^{2+}][Tl^{III}]/[Hg^{II}]$, imply the mechanism

$$Hg_2^{2+} \rightleftharpoons Hg^0 + Hg^{II} \qquad (14)$$

$$Hg^0 + Tl^{III} \rightarrow Hg^{II} + Tl^{I} \qquad (15)$$

The rate constant for the latter step (10^6 l. mole^{-1} sec.$^{-1}$ at 25°) is at least 10^6 times that for direct oxidation of Hg_2^{2+}.[66] The very rapid isotopic exchange between Hg_2^{2+} and Hg^{2+} is also believed[67] to proceed through the dismutation step (14).

In some cases, notably where substitution-inert species are involved, chemical evidence may serve as a guide to mechanism. Thus the observation[68] that Cr^{II} is oxidised to Cr_{aq}^{3+} by 1-equivalent oxidants such as Cu^{II} and Fe^{III} but to a binuclear species (probably $Cr–O–Cr^{4+}$) by 2-equivalent oxidants such as H_2O_2 and Tl^{III} suggests that the latter reaction proceeds through an initial 2-electron transfer:

$$Cr^{II} + Tl^{III} \rightarrow Cr^{IV} + Tl^{I} \qquad (16)$$

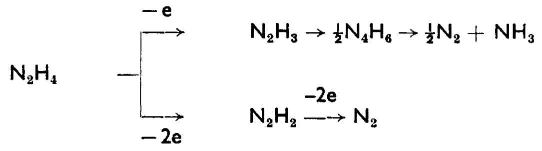
$$Cr^{IV} + Cr^{II} \rightarrow (Cr^{III})_2 \qquad (17)$$

or, alternatively, through a modification of the termolecular mechanism involving a binuclear Cr^{II} species:

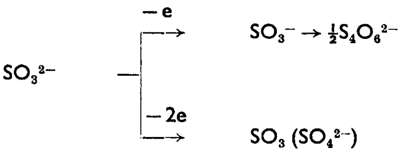
$$2Cr^{II} \rightarrow (Cr^{II})_2 \qquad (18)$$

$$(Cr^{II})_2 + Tl^{III} \rightarrow (Cr^{III})_2 + Tl^{I} \qquad (19)$$

In this connexion reference should also be made to the oxidations of N_2H_4 and SO_3^{2-},[69] which tend to exhibit different stoicheiometries with 1- and 2-equivalent oxidents, *i.e.*:



$$N_2H_4 \begin{cases} \xrightarrow{-e} N_2H_3 \rightarrow \tfrac{1}{2}N_4H_6 \rightarrow \tfrac{1}{2}N_2 + NH_3 \\ \xrightarrow[-2e]{} N_2H_2 \xrightarrow{-2e} N_2 \end{cases}$$



$$SO_3^{2-} \begin{cases} \xrightarrow{-e} SO_3^{-} \rightarrow \tfrac{1}{2}S_4O_6^{2-} \\ \xrightarrow{-2e} SO_3\ (SO_4^{2-}) \end{cases}$$

These systems have proved useful in assessing the relative 1- and 2-equivalent oxidising tendencies of different oxidants.

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[66] Armstrong, Halpern, and Higginson, *J. Phys. Chem.*, 1956, **60**, 1661; Armstrong and Halpern, *Canad. J. Chem.*, 1957, **35**, 1020.

[67] Wolfgang and Dodson, *J. Phys. Chem.*, 1952, **56**, 872.

[68] Arden and Plane, *J. Amer. Chem. Soc.*, 1959, **81**, 3197.

[69] (*a*) Kirk and Brown, *ibid.*, 1928, **50**, 337; Higginson, Sutton, and Wright, *J.*, 1953, 1380, 1402; *J.*, 1955, 1551; (*b*) Higginson and Marshall, *J.*, 1957, 447.

Complementary Reactions (2-Equiv. Oxidant + 2-Equiv. Reductant).—The reactions in this class, of which the Tl^{I}–Tl^{III} exchange[48,41] and oxidation of U^{IV} by Tl^{III} (ref. 70) are typical, commonly exhibit simple bimolecular rate-laws, *e.g.*, $k[U^{IV}][Tl^{III}]$, which are consistent with either a single 2-equivalent step:

$$U^{IV} + Tl^{III} \xrightarrow{k} U^{VI} + Tl^{I} \qquad \ldots\ldots\ldots \quad (20)$$

or with a sequence of 1-electron steps;

$$U^{IV} + Tl^{III} \xrightarrow{k} U^{V} + Tl^{II} \qquad \ldots\ldots\ldots \quad (21)$$

$$U^{V} + Tl^{II} \xrightarrow[\text{Fast}]{} U^{VI} + Tl^{I} \qquad \ldots\ldots\ldots \quad (22)$$

In the limiting case of the second mechanism where the two intermediates react with each other before they can diffuse out of the solvent cage in which they are formed, a direct distinction between the two mechanisms becomes very difficult and of questionable meaning.[71] In more favourable cases, where the intermediates do escape into the surrounding solution their detection (*e.g.*, through some competing reaction) and thus confirmation of a mechanism of the second type becomes, at least in principle, possible.

One of the implications of the comparison on which the principle of equi-valency change is based is that reactions between 2-equivalent oxidants and 2-equivalent reductants occur by a concerted 2-equivalent step for, otherwise, they would be expected to be on the whole even slower than non-complementary reactions. This, and the absence of evidence for the existence of intermediate oxidation states, provide some indirect support for the view that many reactions such as the Tl^{I}–Tl^{III} exchange do proceed by 2-equivalent mechanisms. The entropy correlations discussed by Higginson *et al.*[34] also favour this conclusion, $\Delta S^{\ddagger}$ for the Tl^{+}–Tl^{3+} exchange (~ -20 e.u.) being more negative than that expected for the rate-determining step $Tl^{+} + Tl^{3+} \rightarrow 2Tl^{2+}$ for which ΔS° is probably quite positive. None of this evidence, however, is conclusive and there remains considerable uncertainty about the detailed mechanisms of these reactions.

On the other hand, numerous examples are now known[42] of reactions in which a 2-equivalent redox change is accomplished apparently in a single step through the transfer of a hydride ion (*e.g.*, $R_2CH{\cdot}O^- + MnO_4^- \rightarrow R_2CO + HMnO_4^{2-}$) or of an oxygen atom (*e.g.*, $NO_2^- + OCl^- \rightarrow NO_3^- + Cl^-$). For such reactions at least, if not for reactions of the electron-transfer type, it is now generally recognised that the Michaelis[72] principle of "compulsory univalent oxidation" is without universal validity.

[70] Harkness and Halpern, *J. Amer, Chem. Soc.*, 1959, **81**, 1526.

[71] Westheimer in McElroy and Glass, "Mechanism of Enzyme 'Action," Johns Hopkins Press, Baltimore, 1954, p. 321.

[72] Michaelis, *Trans. Electrochem. Soc.*, 1958, **80**, 1073; *Cold Spring Harbor Symp. Quant. Biol.*, 1939, **1**, 33.

In addition to the simple mechanisms considered above, an inherent possibility for reactions between 2-equivalent oxidants and reductants is a chain mechanism initiated by an initial 1-electron transfer and propagated by the two intermediate oxidation states. An example of this is the oxidation of U^{IV} by oxygen, for which the mechanism (23—26) has been advanced:[73]

Initiation: $U^{IV} + O_2 \rightarrow U^{V} + HO_2$ . . . . (23)

Propagation: $U^{V} + O_2 \rightarrow U^{VI} + HO_2$ . . . . (24)

$U^{IV} + HO_2 \rightarrow U^{V} + H_2O_2$ . . . . (25)

Termination: $U^{V} + HO_2 \rightarrow U^{VI} + H_2O_2$ . . . . (26)

Similar mechanisms apparently operate in the oxidation of other 2-equivalent reductants (*e.g.*, SO_3^{2-}) by oxygen, but not in any known instance of a reaction such as (20) between two metal ions. A factor which may favour this type of mechanism over a direct 2-equivalent reaction in the case of oxygen is the change in spin multiplicity (triplet→singlet) which accompanies the reduction of oxygen to hydrogen peroxide.

Multi-equivalent reactions: Redox reactions in which there is a net transfer of more than two electrons (*e.g.*, those involving the Mn^{II}–Mn^{VII} or Cr^{III}–Cr^{VI} couples) almost certainly proceed by multi-step mechanisms. An example of such a reaction is

$Cr^{III} + 3Ce^{IV} \rightarrow Cr^{VI} + 3Ce^{III}$ . . . . (27)

for which Tong and King[74] found the rate-law, $k[Cr^{III}][Ce^{IV}]^2[Ce^{III}]$-1, suggesting the mechanism,

$Ce^{IV} + Cr^{III} \rightleftharpoons Ce^{III} + Cr^{IV}$ (rapid equil.) . . . . . (27a)

$Ce^{IV} + Cr^{IV} \rightarrow Ce^{III} + Cr^{V}$ (rate-determining) . . . . (27b)

$Ce^{IV} + Cr^{V} \rightarrow Ce^{III} + Cr^{VI}$ (rapid) . . . . . . (27c)

Some Indirect Redox Mechanisms

In some cases redox processes proceed through mechanisms which do not involve direct reaction (*i.e.*, direct transfer of electrons or of oxidizing or reducing groups) between the oxidant and the reductant. Such indirect mechanisms are frequently responsible for catalytic effects in redox systems.

[73] Halpern and Smith, *Canad. J. Chem.*, 1956, **34**, 1419.
[74] Tong and King, *J. Amer. Chem. Soc.*, 1960, **82**, 3805.

Electron release to solvent. One possible alternative to direct electron transfer is the release of an electron by the reductant to the solvent and its subsequent capture by the oxidant, *e.g.*:

$$\mathrm{Cr^{2+} \rightarrow Cr^{3+} + e^-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (28a)$$

$$\mathrm{Fe^{3+} + e^- \rightarrow Fe^{2+}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (28b)$$

This might be expected to occur with the very powerful reducing agents, particularly in solvents such as ammonia which give rise to stable solutions of "electrons". In aqueous or alcoholic solution, electron release would probably result in reduction of the solvent with the formation of a hydrogen atom that could subsequently reduce the oxidant. The reduction of metal ions such as Ag^+ and Fe^{3+} in aqueous solution by hydrogen atoms (generated radiolytically or photochemically or introduced from the gas phase) is indeed well known.[75] There is no experimental evidence, however, that either free electrons or hydrogen atoms are intermediates in redox reactions between metal ions, even with ions as strongly reducing as Cr^{2+}.

Intermediate oxidation or reduction of ligands. Oxidisable or reducible ligands can act in effect as "electron carriers" between metal ions. An example of this is the Br^--catalysed Tl^{I}–Tl^{III} isotopic exchange where kinetic contributions of the forms $k[TlBr_2^+]$ and $k[TlBr_3]$ (in each case zero-order in Tl^{I}) have been identified[41] with the exchange paths

$$\mathrm{TlBr_2^+ \rightleftharpoons Tl^+ + Br_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (29)$$

$$\mathrm{TlBr_3 \rightleftharpoons Tl^+ + Br_2 + Br^-} \quad . \; . \; . \; . \; . \quad (30)$$

Corresponding 1-electron oxidation or reduction of ligands to yield atoms or free radicals (*e.g.*, Br, Cl, or OH) is usually less favourable energetically and such intermediates are not commonly encountered in thermal redox reactions between metal ions. One possible such case is the oxidation of Tl^{I} by Ce^{IV} where hydroxyl, formed by the reaction $CeOH^{3+} \rightleftharpoons Ce^{3+} + OH$, is suggested as an intermediate.[76,58]

Intermediate oxidation or reduction of the bridging ligand (in this case without release from the bridged complex) also constitutes a possible mechanism of electron transfer in inner-sphere bridged complexes,[43] *e.g.*:

$$\begin{tikzcd}
 & (\mathrm{Cr^{3+}\text{–}X^{2-}\text{–}Co^{3+}}) \arrow[dr] & \\
(\mathrm{Cr^{2+}\text{–}X^{-}\text{–}Co^{3+}}) \arrow[ur] \arrow[dr] & & (\mathrm{Cr^{3+}\text{–}X^{-}\text{–}Co^{2+}}) \\
 & (\mathrm{Cr^{2+}\text{–}X\text{–}Co^{2+}}) \arrow[ur] &
\end{tikzcd}$$

Catalysis by metal ions. Ions, such as Cu^{2+} and Ag^+, of metals which exhibit two or more stable oxidation states, may also serve to "transport"

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[75] Collinson, Dainton, Smith, Trudel and Tazuke, *Discuss. Faraday Soc.*, 1960, **29**, 188; Halpern, *ibid.*, 1960, **29**, 252.

[76] Armstrong and Halpern, unpublished work; Gryder and Dorfman, *J. Amer. Chem. Soc.*, 1961, **83**, 1254.

electrons in redox reactions through a chain mechanism in which the catalytic metal ion is successively oxidised and reduced. Such mechanisms are fairly common, some examples being:

(*a*) Catalysis by $\mathrm{Cu^{II}}$ of the reaction,[34] $\mathrm{V^{III} + Fe^{III} \rightarrow V^{IV} + Fe^{II}}$. The rate-law for the catalysed path, $k[\mathrm{V^{III}}][\mathrm{Cu^{II}}]$, suggests the mechanism:

$$\mathrm{V^{III} + Cu^{II}} \xrightarrow{k} \mathrm{V^{IV} + Cu^{I}} \tag{31}$$

$$\mathrm{Cu^{I} + Fe^{III}} \xrightarrow{\text{Fast}} \mathrm{Fe^{II} + Cu^{II}} \tag{32}$$

(*b*) Catalysis by $\mathrm{Ag^{I}}$ of the reaction,[34] $\mathrm{Tl^{I} + 2Ce^{IV} \rightarrow Tl^{III} + 2Ce^{III}}$. The rate-law $k_1k_2[\mathrm{Ce^{IV}}][\mathrm{Tl^{I}}][\mathrm{Ag^{I}}]/(k_{-1}[\mathrm{Ce^{III}}] + k_2[\mathrm{Tl^{I}}])$ is consistent with the mechanism:

$$\mathrm{Ce^{IV} + Ag^{I}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ce^{III} + Ag^{II}} \tag{33}$$

$$\mathrm{Tl^{I} + Ag^{II}} \xrightarrow{k_2} \mathrm{Tl^{II} + Ag^{I}} \tag{34}$$

$$\mathrm{Tl^{II} + Ce^{IV}} \xrightarrow{\text{Fast}} \mathrm{Tl^{III} + Ce^{III}} \tag{35}$$

(*c*) Catalysis by $\mathrm{Cu^{II}}$ of the oxidation of $\mathrm{U^{IV}}$ by oxygen (reaction 23),[73] probably through catalysis of the initiation step (23) by the mechanism:

$$\mathrm{U^{IV} + Cu^{II} \rightarrow U^{V} + Cu^{I}} \tag{36}$$

$$\mathrm{Cu^{I} + O_2 \rightarrow Cu^{II} + O_2^{-}(HO_2)} \tag{37}$$

Other examples where similar mechanisms probably operate are: $\mathrm{Fe^{II} + O_2}$; $\mathrm{V^{III} + O_2}$ (both catalysed by $\mathrm{Cu^{II}}$);[59,77] $\mathrm{MnO_4^{2-}}$–$\mathrm{MnO_4^{-}}$ [catalysed by $\mathrm{Fe(CN)_6^{3-}}$].[65] In all these cases the sequence of electron transfers from reductant to catalyst, and from catalyst to oxidant, is apparently more efficient than direct electron transfer. The reasons for this and for the particularly widespread effectiveness of the $\mathrm{Cu^{I}}$–$\mathrm{Cu^{II}}$ couple in catalytic mechanisms of this type are not altogether clear.

Theoretical Considerations

The theory of electron-transfer reactions in solution has been considered by various authors. Libby[78] attempted to account for some of the observed rate differences in terms of the Franck–Condon principle; a quantitative treatment incorporating some of these ideas was subsequently developed by R. A. Marcus.[79] R. J. Marcus, Zwolinski, and Eyring,[80] Weiss,[81] and

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[77] Ramsey, Sugimoto, and De Vorkin, *J. Amer. Chem. Soc.*, 1941, **63**, 3480.

[78] Libby, *J. Phys. Chem.*, 1952, **56**, 863.

[79] Marcus, *J. Chem. Phys.*, (*a*) 1956, **24**, 966; (*b*) 1957, **26**, 867, 872; (*c*) *Discuss. Faraday Soc.*, 1960, **29**, 21.

[80] Marcus, Zwolinski, and Eyring, *J. Phys. Chem.*, 1954, **58**, 432.

[81] Weiss, *Proc. Roy. Soc.*, 1954, *A*, **222**, 128.

Laidler[82] have given quantitative treatments of electron transfer based on electron-tunnelling models. Orgel[83] has discussed some aspects of the problem from the standpoint of the ligand-field theory. George and Griffith,[84] and Halpern and Orgel,[43] have examined the detailed mechanism of electron transfer between metal ions with particular reference to the role of bridging ligands. Also relevant to the subject are various theoretical considerations relating to the somewhat simpler and better understood electron-transfer processes which occur in the gas phase.[85,86]

The following discussion of the subject, while not complete, summarises many features of the above treatments. The general approach follows, in many respects, that of Marcus.[79]

The treatment of even the simplest type of electron-transfer process in solution is considerably more complicated than that of the corresponding process in the gas phase, in that account must be taken in a rather detailed way, not only of the interactions of the reactants with each other, but also of those with the surrounding medium. The distinction between reactant and medium in this sense is sometimes rather arbitrary. For example, in the reaction,

$$\mathrm{Fe^{2+}aq + {}^{*}Fe^{3+}aq \rightarrow Fe^{3+}aq + {}^{*}Fe^{2+}aq} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (38)$$

the "reactants" may be defined so as to include the inner hydration shells or, alternatively, the latter may be regarded as part of the surrounding medium. Whatever the terminology employed, however, a realistic model must include as part of the reacting system, not only the inner co-ordination shells of the ions, but also that region of the surrounding solvent with which they interact, *i.e.*, that which they polarise or over which the transferring electron is significantly delocalised. Thus even in the simplest cases we are dealing effectively with reactions of rather large and complex "molecules". The fact that the configuration of the transition state, including the compositions of the inner co-ordination shells which may differ from those of the reactants, is frequently not known with certainty further complicates the problem.

In the absence of electronic interaction between the reacting species, the reactants and products, in a reaction such as (38), may be regarded as two different electronic states of the system (represented by the wave functions ϕ_R and ϕ_P), each corresponding to a distinct potential energy surface in a many-dimensional atomic configuration space whose co-ordinates include those of all the atoms of the two reactants and of the surrounding medium. To simplify our discussion we may consider only the first co-ordination shell of each ion, which we assume to consist of six ligand molecules in a

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[82] Laidler, *Canad. J. Chem.*, 1959, **37**, 138.

[83] Orgel, Report X Conseil Chim. Solvay, Brussels, 1956, p. 289.

[84] Griffith and George in Boyer, Lardy and Myrbäck, "The Enzymes," Vol. 1, Academic Press Inc., New York, 1959, p. 347.

[85] Massey and Burhop, "Electron and Ionic Impact Phenomena", Oxford University Press, 1952.

[86] Gurnee and Magee, *J. Chem. Phys.*, 1957, **26**, 1237.

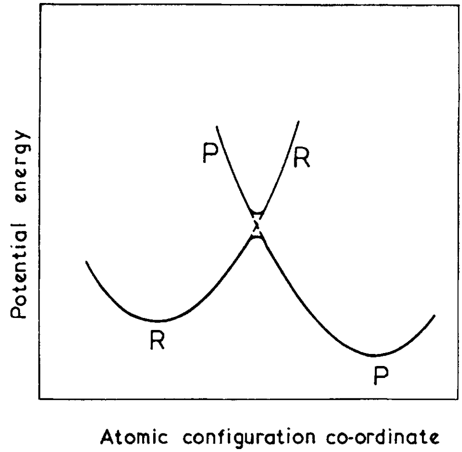

FIG. 2. *Schematic potential energy diagram (after Marcus).*

regular octahedral arrangement. Our system then will have three atomic configuration co-ordinates, the two metal–ligand separations and the separation between the centres of the two ions. Since the first two of these have different equilibrium values for the reactants and products [*e.g.*, the equilibrium Fe–O separations in $Fe(OH_2)_6^{3+}$ and $Fe(OH_2)_6^{2+}$ differ by about 0·15 Å], the two potential energy surfaces will have minima in different regions of atomic configuration space. In general, however, there will also be a region of intersection of the surfaces, corresponding to non-equilibrium atomic configurations, in which the energies of the two electronic states are equal. The situation is depicted schematically in Fig. 2 where a single atomic configuration co-ordinate is used. A more complete treatment would take account, not only of the first co-ordination shell, but also of the polarisation of the surrounding solvent which will differ for the two states.

Electronic interaction between the two states, without which transition between them would not occur, leads to the usual splitting of the surfaces as indicated in Fig. 2. Instead of two intersecting surfaces we now have an upper and a lower surface, separated in the vicinity of the hypothetical intersection region by twice the interaction energy, H_{RP} ($= <\phi_R|H|\phi_P>$), of the two states. The qualitative behaviour which ensues depends to some extent on the magnitude of this interaction energy and it is convenient to consider three different cases.

(1) *Non-adiabatic electron transfer.* This corresponds to the case of very weak interaction of the two states (*e.g.*, when the reactants are very far apart or when the reactants and the products have different spin multiplicities) so that splitting of the surfaces is negligible. Because of the Franck–Condon restriction, a radiationless transition between the two

states can occur only in the vicinity of the intersection region where their energies are equal.* Thus there must occur, *before* electron transfer, a rearrangement of the atomic configuration of the system to some non-equilibrium (*i.e.*, vibrationally excited) configuration, usually intermediate between that of the reactants and the products. The energy required for this has been denoted the Franck–Condon reorganisation energy.

In such a case the apparent free energy of activation can be regarded, to a first approximation, as made up of the three contributions, namely:

$$\Delta F\ddagger = \Delta F\ddagger_{\text{rep}} + \Delta F\ddagger_{\text{reorg}} - RT \ln \kappa \quad . \; . \; . \; . \quad (39)$$

where $\Delta F\ddagger_{\text{rep}}$ is the free energy of repulsion between the reactants in the activated complex, $\Delta F\ddagger_{\text{reorg}}$ is the Franck–Condon reorganisation free energy, and κ is a transmission coefficient representing the probability that the system will remain on the lower surface (*i.e.*, that electron transfer will occur) when it passes through the intersection region. When this probability is small, κ is given[6] by:

$$\kappa = 1 - \exp\left[\frac{-4\pi^2 H_{\text{RP}}}{hV|S_{\text{R}} - S_{\text{P}}|}\right] \approx \frac{4\pi^2 H^2{}_{\text{RP}}}{hV|S_{\text{R}} - S_{\text{P}}|} \quad . \; . \; . \quad (40)$$

where $|S_{\text{R}} - S_{\text{P}}|$ is the difference of slopes of the crossing potential surfaces, V is the velocity of crossing, and H_{RP} is the interaction energy at the crossing point.

The intersection surface will, of course, extend over many configurations of the system corresponding, for example, to different separations of the reacting ions. For ions of the same sign, both $\Delta F\ddagger_{\text{rep}}$ and κ will in general decrease with increasing separation, with opposing effects on $\Delta F\ddagger$. In the activated complex of most favourable configuration, *i.e.*, that for which $\Delta F\ddagger$ is a minimum, the separation between the exchanging ions will thus correspond to the best compromise between the electrostatic repulsion resisting close approach of the ions and the low probability of electron transfer at large separations.

The quantities in equation (39), particularly κ, are not readily computed for systems as complex as those of actual interest. Some calculations have been attempted for the Fe^{2+}–Fe^{3+} and related exchange reactions, approximating κ by the probability of electron tunnelling though a potential barrier of some assumed shape.[80,82] These treatments are necessarily very approximate, and based in some cases on models of questionable validity, but the results serve to emphasise at least qualitatively some features of the behaviour described above.

(2) *Adiabatic transfer: weak interaction.* This corresponds to the limiting case, where electronic interaction between the reactants in the

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* The Franck–Condon restriction applies also to electron transfer between polyatomic species in the gas phase. It has been estimated,[86] for example, that the cross-section of the H_2–H_2^+ and N_2–N_2^+ electron transfers are reduced by factors of 0·31 and 0·94, respectively, owing to the different equilibrium internuclear separations of the molecules and corresponding ions.

activated complex is sufficient for the system to remain on the lower surface when it passes through the intersection region (*i.e.*, $\kappa \approx 1$), yet weak enough for the contribution of the interaction energy to the lowering of the activation energy to be neglected. The products are now formed from the reactants adiabatically, yet the splitting of the surfaces is small, so that to a good degree of approximation the activated complex can be identified with the lowest crossing point of the hypothetical non-interacting surfaces and $\Delta F\ddagger$ can be computed without explicitly evaluating the interaction energy. Marcus[79] suggested that this approximation (which requires that the interaction energy in the activated complex lie within a rather narrow range, roughly between 0·01 and 1 kcal./mole) is valid for many actual electron-transfer reactions in solution and has developed a quantitative theory based on it. In its original form this makes the further simplifying approximations.

(*a*) Each reactant (*i.e.*, the metal ion plus its co-ordination shell) is treated as a rigid sphere, inside which no changes in interatomic distances occur during the reaction. Thus only reorganisation of the surrounding medium, which is treated as a continuous unsaturated dielectric, contributes to $\Delta F\ddagger_{\text{reorg}}$.

(*b*) The separation, r_{12}, between the centres of the two reactants in the activated complex is taken as equal to the sum of their radii ($r_1 + r_2$).

This leads to the following expression for $\Delta F\ddagger$, where the first term corresponds to $\Delta F\ddagger_{\text{rep}}$ and the second to $\Delta F\ddagger_{\text{reorg}}$:

$$\Delta F\ddagger = \frac{e_1 e_2}{D_s r_{12}} + m^2\lambda \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (41)$$

where
$$2m + 1 = -\left(\Delta F^\circ + \frac{e_1 e_2 - e_1' e_2'}{D_s r_{12}}\right)\Big/\lambda \quad . \; . \; . \; . \quad (42)$$

$$\lambda = (\Delta e)^2\left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{r_{12}}\right)\left(\frac{1}{\eta^2} - \frac{1}{D_s}\right) \quad . \; . \; . \; . \quad (43)$$

e_1, e_2 are the reactant charges and e_1', e_2' the product charges, Δe $(= e_1' - e_1)$ is the number of electrons transferred, ΔF° is the standard free energy of the electron transfer step, η is the refractive index of the solvent, and D_s is the static dielectric constant.

For an isotopic exchange reaction, where $\Delta F^\circ = 0, e_1 = e_2', e_2 = e_1'$, $r_1 = r_2 = r$, equation (41) reduces to

$$\Delta F\ddagger = \left[\frac{e_1 e_2}{D_s} + \frac{(\Delta e)^2}{4}\left(\frac{1}{\eta^2} - \frac{1}{D_s}\right)\right]\frac{1}{2r} \quad . \; . \; . \; . \quad (44)$$

Values of $\Delta F\ddagger$ for several reactions computed from this expression are listed in Table 4. Reasonable agreement with experiment is found for reactions of covalent complexes such as MnO_4^{2-}–MnO_4^-, $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$, but for the aquo-ions $\Delta F‡_{calc}$ is considerably too low. This probably reflects the larger error introduced in the latter cases by failure to take account of the reorganisation of the inner co-ordination shells.* The assumption of adiabatic electron transfer (*i.e.*, $\kappa = 1$) represents another possible source of error in these calculations which is more likely to be serious for aquo-ions than for complexes such as cyanides in which the *d*-electrons are extensively delocalised.

TABLE 4. *Comparison of calculated and experimental $\Delta F‡$ values.*

Reaction	(Å)	Temp.	$\Delta F‡$ (exp) (kcal./mole)	$\Delta F‡$ (calc) (kcal./mole)	($\Delta F‡_{rep}$/ $\Delta F‡_{reorg}$)	Ref.
MnO_4^{2-}–MnO_4^-	2·9	1°	12·8	9·2	0·17	79*b*
$Fe(CN)_6^{4-}$–$(FeCN)_6^{3-}$	4·5	4	12·7	10·1	1·0	79*b*
Fe^{2+}–Fe^{3+}	3·4	0	16·3	9·8	0·5	79*b*
Co^{2+}–Co^{3+}	3·4	0	16·4	9·9	0·5	79*b*
$Fe(C_5H_5)_2$–$Fe(C_5H_5)_2^+$	4·10	−75	6·0	5·3	—	14
,, ,,	3·54	−75	6·0	6·1	—	14

More recently Marcus[79c] has extended the theory to take account also of reorganisation of the first co-ordination shell and of electrolyte effects, but these refinements have not as yet been quantitatively applied.

(3) *Adiabatic transfer: strong interaction.* This corresponds to the situation which prevails in ordinary chemical reactions where covalent bonds are broken and new ones simultaneously formed. Redox reactions which proceed through the transfer of covalently bonded atoms (*e.g.*, oxygen atoms or hydride ions) belong in this category, as do electron-transfer reactions between metal ions which are strongly coupled by inner-sphere bridging ligands. In such cases lowering of the activation energy, by interaction between the reactants in the transition state, is likely to be appreciable and cannot be neglected. Absolute rate calculations, as with ordinary chemical reactions, thus become prohibitively difficult. A quantitative treatment of electron transfer, based on a similar model has also been formulated by Hush.[88]

Factors Affecting Rates of Electron Transfer.—Perhaps of greater significance than the rather restricted quantitative applications of the theoretical treatments cited above is the qualitative insight which they have provided into the factors which affect the rates and mechanisms of electron-transfer reactions and which account for some of the observed trends. Among these are the following.

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* Corrected values of $\Delta F‡_{calc.} = 18$ kcal./mole which include the reorganisation free energies of the first co-ordination shells, have been reported[87] for the Fe^{2+}–Fe^{3+} and the Co^{2+}–Co^{3+} reaction. Although details of the calculations were not given, the method used is probably that described in Ref. 79*c*.

[87] Marcus, Trans. New York Acad. Sci., 1957, **19**, 423.

[88] Hush, *Discuss. Faraday Soc.*, 1960, **29**, 113, 116.

(1) *Electrostatic repulsion.* Both theoretical and experimental considerations suggest that $\Delta F^{\ddagger}_{\text{rep}}$ (given by e_1e_2/D_sr) is usually small, at least for reactions of the outer-sphere type in aqueous solution. Thus there appears to be no widespread correlation between rates of electron-transfer reactions and the charges of the reacting ions, and many reactions between highly charged ions of the same sign are very fast, *e.g.*, $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$, Fe $phen_3^{2+}$–Fe $phen_3^{3+}$. For the reactions listed in Table 3 the contributions of $\Delta F^{\ddagger}_{\text{rep}}$ to the total $\Delta F^{\ddagger}_{\text{calc}}$ range from 15 % to 50 %. In inner-sphere reactions, however, because of the closer approach of the metal ions, Coulomb repulsion between them may become more important, particularly when the bridging ligand is uncharged. The very large difference ($\sim 10^6$-fold) between the rates of oxidation of Cr^{2+} by $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5OH^{2+}$ is undoubtedly due in part to this. Also, because of the dependence of $\Delta F^{\ddagger}_{\text{rep}}$ on the dielectric constant, this factor is likely to become more important in passing from water to less polar media; this may account, at least in part, for the generally slower rates of electron transfer in non-aqueous solutions.

(2) *Reorganisation energy.* The theoretical predictions concerning the importance of this factor are well borne out by experimental evidence. In general, slow electron transfer is observed when the reactants and products differ appreciably in atomic configuration, *i.e.*, in the geometries or dimensions of their co-ordination shells. In recent years the ligand-field theory[83] has contributed greatly to our understanding of this factor as it affects the reactions of transition-metals ions and complexes. This theory leads to the expectation of larger changes in metal–ligand bond lengths, and hence larger reorganisation energies for the transfer of e_g than of t_{2g} *d*-electrons between octahedral complexes. This factor undoubtedly accounts for the very slow electron transfer between Cr^{2+} and Cr^{3+}, compared with, say, V^{2+}–V^{3+} or Fe^{2+}–Fe^{3+}.

(3) *Electron "conductivity" of ligands.* Unlike simple electron-transfer reactions between atomic species in the gas phase, which depend on direct overlap of the donor and acceptor atomic orbitals, reactions between metal ions generally involve electron transfer through intervening ligand and/or solvent molecules. The electronic interactions which determine the probability of electron transfer in such systems are thus rather complex and at best only qualitatively understood.[43] In a general way we expect the ease of electron transfer to depend on the extent of delocalisation of the donor and acceptor metal orbitals in the activated complex, through mixing with orbitals of the intervening ligands.* From this standpoint ligands, such as water and ammonia, which contain saturated single bonds

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* Recent investigations of the nuclear magnetic and paramagnetic resonance spectra of transition-metal compounds provide direct information about this. Thus it is found that even in highly ionic substances such as MnF_2, the unpaired *d*-electrons of the metal are partly delocalised (to the extent of 5—10 %) over the surrounding fluoride ions.[89]

[89] Owen, *Discuss. Faraday Soc.*, 1958, **26**, 53.

are expected to be much less effective in "conducting" electrons between metal ions than unsaturated ligands, such as CN^-, and phenanthroline whose complexes are characterised by a high degree of covalency and electron delocalisation. While the experimental evidence cited (Table 1) is, on the whole, in accord with this, the comparisons involved (*e.g.*, Fe_{aq}^{2+}–Fe_{aq}^{3+} and Fe $phen_3^{2+}$–Fe $phen_3^{3+}$) are complicated by the fact that the geometrical configurations of the two oxidation states usually differ less in complexes of the latter type than in those of the former, so that differences in reorganisation energy also contribute to the observed rate differences. Since the two effects arise to a large extent from related causes, they are not readily separated experimentally and their relative importance is difficult to assess.

(4) $\Delta F°$. Equation (42) implies that the free energy, $\Delta F°$, of reaction of the electron-transfer process, enters into determination of the rate. The following physical interpretation may be placed on this: where there is an overall decrease in free energy, the requirement for atomic rearrangement before electron transfer (*i.e.*, $\Delta F\ddagger_{\text{reorg}}$) is reduced, since the product may now be formed in vibrationally excited states, without the need for corresponding excitation of the reactants, and the excess of vibrational free energy is dissipated as part of the overall free energy of reaction.

The experimental evidence is, on the whole, in accord with this prediction. Thus, electron-transfer reactions between dissimilar ions in which there is a net free-energy decrease are in general faster (often too fast to measure) than the isotopic exchange reactions of either ion, *e.g.*, the oxidation of Fe^{II} by Ce^{IV} is faster than either the Fe^{II}–Fe^{III} or the Ce^{III}–Ce^{IV} isotopic exchange. It has been suggested[90] that some of the variations (Table 1) in the rate of oxidation of Cr^{2+} by different Co^{III} complexes [*e.g.*, $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5OH_2^{3+}$] are also due to this factor. Good correlations between $\Delta F\ddagger$ and $\Delta F°$ are exhibited by several series of redox reactions including electron transfer between Fe^{2+} and different $Fe^{(III)}$ complexes,[28,91] as well as the oxidations of leucoindophenols by oxygen and of quinols by Fe^{3+} which are believed to involve electron-transfer mechanisms[79b] In other cases, already cited, correlations between $\Delta S\ddagger$ and $\Delta S°$ and between $\Delta H\ddagger$ and $\Delta H°$ have been observed.

(5) *Multiple-electron transfers.* As noted earlier, there is some uncertainty as to whether 2-electron transfer reactions such as the Tl^{I}–Tl^{III} exchange occur in a single step or through successive 1-electron steps. The choice of mechanism in such cases will be influenced by the following factors.

(*a*) Differences in $\Delta F°$. In reactions between 2-equivalent oxidants and 2-equivalent reductants these will normally be in the direction of favouring concerted 2-electron transfer.

[90] Shimi and Higginson, *Discuss. Faraday Soc.*, 1960, **29**, 122.
[91] Ford-Smith and Sutin, *J. Amer. Chem. Soc.*, 1961, **83**, 1830.

(*b*) The lower probability of a 2-electron transition. While this has often been cited as an argument against 2-electron transfers, there are grounds for questioning its general validity. Thus, 2-electron-transfer processes such as $A + A^{2+} \rightarrow A^{2+} + A$ and $Ne + Ne^{2+} \rightarrow Ne^{2+} + Ne$ are known to occur in the gas phase with cross-sections only slightly lower ($\frac{1}{4}$ to $\frac{1}{2}$ in the cases cited) than those of corresponding resonant 1-electron transfers.[86] A greater reduction in the relative probability of 2-electron transfer is, however, expected where interaction between the reactants in the activated complex is very weak, *i.e.*, for reactions proceeding by a non-adiabatic mechanism.

(*c*) Differences in $\Delta F^{\ddagger}_{\text{reorg}}$. A greater difference in configuration, and hence a larger reorganisation energy, are expected when the two oxidation states differ by two electrons than when they differ by one. This is reflected in the $(\Delta e)^2$ term in equation (43), which implies four times as large a $\Delta F^{\ddagger}_{\text{reorg}}$ for a 2-electron transfer as for a corresponding 1-electron transfer.

Because the other factors become relatively less important in such cases, (*a*) is likely to dominate in reactions which proceed through strong-interaction activated complexes, *e.g.*, by oxygen atom or hydride transfer, or by inner-sphere bridged mechanisms. Indeed, such mechanisms are commonly encountered in 2-equivalent redox reactions. On the other hand, with "weak-interaction" activated complexes, $\Delta F^{\ddagger}_{\text{reorg}}$ often makes the dominant contribution to the overall free energy of activation and in such cases [especially with reactions proceeding by non-adiabatic mechanisms where (*b*) also becomes important] 1-electron transfers are likely to be preferred. For the Tl^{+}–Tl^{3+} and related reactions, particularly in the absence of a knowledge of the thermodynamic and other relevant properties of Tl^{2+}, the relative importance of the various factors is difficult to assess and the mechanisms in these cases remain uncertain.

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