ON THE THEORY OF OXIDATION-REDUCTION REACTIONS INVOLVING ELECTRON TRANSFER. V. COMPARISON AND PROPERTIES OF ELECTROCHEMICAL AND CHEMICAL RATE CONSTANTS[1]

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Using a theory of electron transfers which takes cognizance of reorganization of the medium outside the inner coördination shell and of changes of bond lengths inside it, relations between electrochemical and related chemical rate constants are deduced and compared with the experimental data. A correlation is found, without the use of arbitrary parameters. Effects of weak complexes with added electrolytes are included under specified conditions. The deductions offer a way of coördinating a variety of data in the two fields, internally as well as with each other, and a way of predicting results in one field from those in another. For example, the rate of oxidation or reduction of a series of related reactants by one reagent is correlated with that of another and with that of the corresponding electrochemical oxidation-reduction reaction, under certain specified conditions. These correlations may also provide a test for distinguishing an electron from an atom transfer mechanism.

In recent years many rate constants of electron transfer reactions in solution and at electrodes have been measured,[3,4] and some quantitative comparison of the data in the two fields now seems appropriate. As a guide we shall employ a theory formulated in earlier papers.[5] This theory yielded an expression for the rates of each of these processes, taking into consideration the solvent reorganization occurring outside the inner coördination shell of each reactant prior to (and necessary for) electron transfer.[5a-d]

The theoretical rate constant for either process was given by eq. 1–3[5c,g]

$$k = Ze^{-\Delta F^*/RT} \tag{1}$$

where

$$\Delta F^* = w + m^2\lambda \tag{2}$$

and

$$m = -\left(\frac{1}{2} + \frac{\Delta F^0 + w^p - w}{2\lambda}\right) \tag{3}$$

In eq. 1 Z is the collision frequency of (hypothetical) uncharged species in solution. It will be taken to be $\sim 10^{11}$ l. mole^{-1} sec.$^{-1}$ and $\sim 10^4$ cm. sec.$^{-1}$ for homogeneous and electrochemical reactions, respectively. w is the work needed to bring the two reactants (or reactant plus electrode) together and w^p is the corresponding term for the products. ΔF^0 is the "standard" free energy of the elementary electron transfer step *in the prevailing electrolyte medium.* It is $-nF\eta_a$ for the electrode case. (n = number of electrons transferred; η_a = activation overpotential.) λ was given by eq. 10 in ref. 5c, which is reproduced in eq. 5 below.

More recently this theory was extended to include the effect of changes (Δq_j^0, below) in bond distances and bond angles in the inner coördination shell of each reactant.[5e,f] Equations 1 to 3 were again obtained with λ now equal to

$$\lambda = \lambda_o + \lambda_i \tag{4}$$

λ_o (λ_{outer}) depends on the size and shape of the reactants. For spherical particles undergoing a homogeneous reaction, λ_o is given by eq. 5 below, and for a spherical reactant undergoing an electrochemical reaction it is one-half that expression. λ_i (λ_{inner}) is given by eq. 6 where k_j and k_j^p denote the force constant of the jth vibrational coördinate in a species involved in the reaction when that species is a reactant and when it is a product, respectively. The summation is over both reactants in the homogeneous case and over the one reactant in the electrode one. A rather general expression for the inner shell reorganization barrier is given in ref. 5e, but this one suffices for the purpose of this paper. A more general but formal expression for λ_0, based on statistical mechanics rather than on a dielectric continuum treatment, is given in part VI.[5h]

$$\lambda_o = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)(ne)^2 \tag{5}$$

$$\lambda_i = \Sigma_j \frac{k_j k_j^p}{k_j + k_j^p}(\Delta q_j^0)^2 \tag{6}$$

a_1 and a_2 are the radii of the spherical particles undergoing reaction, the inner coördination shell of each particle being included in the estimation of a_1 and a_2. r is the mean distance between the centers of the reactants in the activated complex. (We take $r = a_1$

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(3) For detailed reviews of homogeneous reactions, see (a) N. Sutin, *Ann. Rev. Nuclear Sci.*, **12**, 285 (1962), and (b) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961).

(4) For detailed summary of electrode kinetic data, see (a) N. Tanaka and R. Tamamushi, "Kinetic Parameters of Electrode Reaction," a report presented to the Commission on Electrochemical Data of the Section of Analytical Chemistry of I.U.P.A.C., at the International Congress of Pure and Applied Chemistry, Montreal, 1961. Copies are obtainable from H. Fischer, Department of Electrochemistry, Institute of Technology, Karlsruhe, Germany. (b) J. Jordan and N. A. Stalica, in "Handbook of Analytical Chemistry," L. Meites, Ed., McGraw-Hill Book Co., New York, N. Y., 1963.

(5) R. A. Marcus (a) *J. Chem. Phys.*, **24**, 966 (1956); (b) O.N.R. Technical Report No. 12. Project NR 051-331 (1957); (c) *Can. J. Chem.*, **37**, 155 (1959); (d) "Trans. Symposium Electrode Processes," E. Yeager, Ed., John Wiley and Sons, New York, N. Y., 1961, p. 239; (e) *Discussions Faraday Soc.*, **29**, 21 (1960); eq. 6 below is actually obtained in ref. 5h, by simplifying those in part IV; (f) unpublished results for the electrochemical case, analogous to those in (e). Equation 9 of the present paper, which is a convenient approximation to the results obtained in sections (ii) and (iii) of ref. 5e, will be discussed in detail in part VI.[5h] As will be pointed out in ref. 5h, there is also a relatively minor reorganization term for the surrounding electrolyte but one which does not alter the correlations in this paper. For brevity, we have omitted it in the present paper. (g) Note on eq. 1 to 3: in a notational change to conform with ref. 5e, w^* and w in ref. 5c are now written as w and w^p, respectively. The factor of 1/2 in eq. 8 of ref. 5c is now incorporated in the present definition of λ_0 for the electrode system, and "e" has been replaced by its molar equivalent, the Faraday F. The values of Z in the present paper are the gas kinetic values. (h) *J. Chem. Phys.*, to be submitted.

$+ a_2$.) In the electrochemical case a_1 and a_2 are equal and r is twice the distance from the center of the reacting particle to the electrode surface. D_{op} and D_s are the square of the refractive index and static dielectric constant, respectively.

For making the correlation described in this paper, an essential feature of eq. 4 to 6 is that

$$\lambda_{soln} = \lambda_1 + \lambda_2 - \lambda_r \qquad (7)$$

where λ_1 depends on the properties of particle 1 (size, force constants, difference of corresponding equilibrium bond distances in reactant and product state) and not on those of particle 2. Similarly, λ_2 depends only on properties of 2. λ_r is the r term in eq. 5. In the electrochemical case we find

$$\lambda_{el} = \lambda_1 - \frac{\lambda_r}{2} \qquad (8)$$

where the value of λ_r in eq. 8 will be equal to or less than that in eq. 7, according as the reacting species can or cannot penetrate any bound layer of solvent molecules adjacent to the electrode surface.[5c]

Particularly pertinent to the following arguments is eq. 9, obtained from eq. 2 and 3 when $|(\Delta F^0 + w^p - w)/\lambda|$ is small (say, 1/4).

$$\Delta F^* \cong \frac{w + w^p}{2} + \frac{\lambda}{4} + \frac{\Delta F^0}{2} \qquad (9)$$

ΔF^* is then linear in ΔF^0 with a slope of 0.5. When w and w^p are small, λ is seen to be four times the value of ΔF^* when $\Delta F^0 = 0$, *i.e.*, $4(\Delta F^*)_0$ say. Thus, the above condition for linearity in ΔF^0 can be written as

$$\left|\Delta F^0/(\Delta F^*)_0\right| \leqslant 1 \qquad (10)$$

a condition often fulfilled in practice.[6] More generally, the *instantaneous* slope of a plot of ΔF^* *vs.* ΔF^0 is, according to eq. 2 and 3, $^1/_2[1 + \Delta F^0/4(\Delta F^*)_0]$ when the work terms are small.

Effect of Standard Free Energy of Reaction or of Overpotential on Reaction Rate.—Two immediate deductions may be drawn from eq. 9 when the work terms can either be made small, say by using high electrolyte concentration, or when they are essentially constant in the following variations: In the oxidation–reduction reaction of a series of related compounds with a given reagent such that ΔF^0 is essentially the only parameter varied, a plot of ΔF^* *vs.* ΔF^0 and hence of log k *vs.* log K should be linear with a slope of 0.5 for ΔF^0's satisfying eq. 10. In the electrochemical case, the corresponding plot of ΔF^* *vs.* $- nF\,\eta_a$ (or of $-RT/nF$ ln k *vs.* electrode potential) should also be linear with a slope of 0.5. The first deduction, predicted first in ref. 5e, was recently confirmed experimentally for the homogeneous oxidation of Fe(II) by a series of substituted $Fe(phen)_3^{+3}$ ions.[7] Again, the slope of the electrochemical plot of RT/nF ln k *vs.* electrode potential is the so-called electrochemical "transfer coefficient." At appreciable salt concentrations transfer coefficients have been found to be near 0.5 (0.4 to 0.6),[8] in agreement with the second deduction.

By analogy, we shall call the slope of the ΔF^* *vs.* ΔF^0 plot the "chemical transfer coefficient" of the reaction.

Two deductions may also be made on the direct relation between electrochemical and related chemical rate constants:

Comparison of Isotopic Exchange Rate and Corresponding Electrochemical Exchange Current.—For an isotopic exchange reaction between ions differing only in valence state, $\Delta F^0 = 0$, $w = w^p$, and hence $m = -0.5$ in eq. 3. In the "exchange current" of the corresponding electrochemical system $\eta_a = 0$ by definition, and $m = -0.5$, if the work term $w - w^p$ is small. The λ_1's and λ_2's in eq. 7 and 8 are all equal. According to the remarks following eq. 8, it then follows that $\lambda_{ex} \leqslant 2\,\lambda_{el}$ (= or < according as the reactant can or cannot penetrate the solvent layer adjacent to the electrode). From a physical viewpoint, the factor of two enters in the exchange system because two ions and their solvation shells are undergoing rearrangement in forming the activated complex while in the electrochemical system there is but one such particle. It thus follows that $\Delta F_{ex}^* \leqslant 2\Delta F_{el}^*$ when w and w^p are small in both the ex and el experiments. From eq. 1 we then expect that $\sqrt{k_{ex}/10^{11}} \geqslant k_{el}/10^4$, where k_{ex} and k_{el} are in units of l. mole sec.$^{-1}$ and cm. sec.$^{-1}$, respectively. Another factor tending to favor the ">" sign is the existence, if any, of inactive sites on the electrode due, say, to any strongly absorbed foreign particles.

More recently it has been concluded theoretically that under certain conditions neither the above deduction of this $\sqrt{k_{ex}}/k_{el}$ relation nor that of the 0.5 slopes of the ΔF^* plots should be affected if one or both of the reactants form relatively weak complexes with other ions.[9] (The ΔF^*'s are then those corresponding to the

(6) *E.g.*, in ref. 7, the intercept of Fig. 2 yields $(\Delta F^*)_0 \sim 12$ kcal. mole^{-1}. (Ref. 7 gives $\Delta F^{\ddagger}$'s but $\Delta F^* = \Delta F^{\ddagger} - RT \ln hZ/kT = \Delta F^{\ddagger} - 2.8$ kcal. mole^{-1} when the standard state in $\Delta F^{\ddagger}$ is 1 mole liter^{-1}.)[5a] Since the largest $|\Delta F^0|$ there was 12 kcal. mole^{-1}, (10) is fulfilled. Again, in electrochemical systems in which the transfer coefficient is measured over an electrode potential range of perhaps 0.2 volt from the equilibrium potential, and in which the typical $(\Delta F^*)_0$ (value of ΔF^* at $\eta_a = 0$) in Table I is of the order of 7 kcal. mole^{-1}, condition (10) is again fulfilled since $|\Delta F^0/(\Delta F^*)_0| \sim 0.2 \times 23/7$.

(7) M. H. Ford-Smith and N. Sutin, *J. Am. Chem. Soc.*, **83**, 1830 (1961). The data satisfy condition (10).[6] It is assumed that in the first approximation the substituents leave the k_j's and Δq_j^0's unaltered. Still more extensive data supporting this predicted value of the slope have been obtained by N. Sutin and collaborators (private communication).

(8) Data are largely but not entirely taken from ref. 4a. The transfer coefficients are either those of the reduction process or are (1-transfer coefficient of the oxidation step): Fe(II)–Fe(III) in 1 *M* H_2SO_4 0.42,[a,b] 0.62,[c] 0.61[c]; $Fe(CN)_6^{-4,-3}$ in 1 *M* KCl 0.45,[c] 0.50,[c] and (graphite) 0.5[d]; V(II)–V(III) in 1 *M* $HClO_4$ 0.52,[e] 0.50 to 0.57,[f] and in 1 *M* H_2SO_4 0.46[f]; Tl(I)–Tl(II) in 1 *M* $HClO_4$ 0.5[g]; Tl(III)–Tl(II) in 1 *M* $HClO_4$ 0.5.[g]

At lower supporting electrolyte concentration: Fe(II)–Fe(III) in 0.1 *M* $HClO_4$, 0.78[h]; $Cr(CN)_6^{-3,-4}$ in 0.2 *M* NaCN 0.67.[i] (The exchange current in the latter system was very sensitive to salt concentration.)

Low values are: Ce(III)–Ce(IV) in 1 *N* H_2SO_4, 0.25,[b] and Mn(II)–Mn(III) in 15 *N* H_2SO_4, 0.28.[a,b] (a) R. Parsons, "Handbook of Electrochemical Constants," Butterworths, London (1959); (b) K. J. Vetter, "Electrochemische Kinetik," Springer-Verlag, 1961; (c) M. D. Wijnen and W. M. Smit, *Rec. trav. chim.*, **79**, 289 (1960); (d) A. Regner and J. Balej, *Collection Czechoslov. Chem. Commun.*, **26**, 237 (1961); (e) K. M. Joshi, W. Mehl, and R. Parsons, "Trans. Symposium Electrode Processes," E. Yeager, Ed., John Wiley and Sons, New York, N. Y., 1961, p. 249; (f) J. E. B. Randles, *Can. J. Chem.*, **37**, 238 (1959); (g) H. Catherino and J. Jordan, private communication; (h) J. Jordan and R. A. Javick, *Electrochim. Acta*, **6**, 23 (1962); (i) P. Delahay and M. Kleinerman, *J. Am. Chem. Soc.*, **82**, 4509 (1960).

(9) R. A. Marcus (unpublished). The conditions imposed in the derivation were that (i) for every pair of reacting complexes the corresponding ΔF^* for electron transfer between the pair is in the linear ΔF^0 region described earlier; (ii) the added ions do not act as bridging groups to any appreciable extent; and (iii) dissociation of any complex does not constitute an important reaction coördinate at the intersection surface of ref. 5e, though it can occur before or later; see, in part, ref. 5h.

If A and B denote different reactants, A^p and B^p the corresponding products, and X and Y any ions forming complexes with these species, condition (i) is fulfilled only if the standard free energy of reaction of $AX_m + BY_n \rightleftarrows A^pX_m + B^pY_n$, ΔF_{mn}^{0xy}, satisfies condition (10) for every important

TABLE I

COMPARISON OF ISOTOPIC EXCHANGE AND ELECTROCHEMICAL RATE CONSTANTS FOR ONE-ELECTRON TRANSFERS AT 25°

System	Medium	$\sqrt{k_{ex}/10^{11}}$	$k_{el}/10^4$	Electrode	Reference
$Fe(CN)_6^{-3,-4}$	1 M K^+	(1×10^{-3})	1×10^{-5}	Pt	a
$MnO_4^{-1,-2}$	0.9 M Na^+	2×10^{-4}	$\sim 2 \times 10^{-5}$	Pt, see ref. 11	b
$Fe^{+2,+3}$	1 M $HClO_4$	9×10^{-6}	7×10^{-7}	Pt	c
$V^{+2,+3}$	1 M $HClO_4$	4×10^{-7}	4×10^{-7}	Hg	d
$Eu^{+2,+3}$	1 M Cl^-	6×10^{-8}	3×10^{-8}	Hg	e
$Tl^{+1,+3}$	1 M $HClO_4$	3×10^{-8h}	2×10^{-8}	Pt	f
$Co(NH_3)_6^{+2,+3}$	0.14 M H^+	$<5 \times 10^{-11}$	$\sim 5 \times 10^{-12}$	Hg	g

Exchange data: [a] Reference 10; [b] J. C. Sheppard and A. C. Wahl, *J. Am. Chem. Soc.*, **79**, 1020 (1957); [c] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952); [d] K. V. Krishnamurty and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 5921 (1958); [e] D. J. Meier and C. S. Garner, *J. Phys. Chem.*, 56, 853 (1952); [f] E. Roig and R. W. Dodson, *ibid.*, **65**, 2175 (1961). [g] See Appendix II. Electrochemical data: [a] Reference 8c; [b] Reference 11; [c] J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 937 (1952); [d] Ref. c, J. E. B. Randles, *Can. J. Chem.*, **37**, 238 (1959), ref. 8i; [e] Ref. c: note that the corresponding isotopic exchange data were insensitive to (H^+), so this comparison could be made; [f] Ref. 8g. See Appendix I. All data are corrected to 25° and to the cited salt concentration listed under "Medium." [g] See Appendix II. [h] Assuming exchange proceeds *via* two one-electron transfers. Otherwise, value is an upper limit for the one-electron transfer rate.

TABLE II

RELATIVE REDUCTION RATES OF $Co(NH_3)_5X$ (III)

X	V^{+2}	$Cr(dipy)_3^{+2}$	DME[a]
NH_3	1	1	1
H_2O	135	91	124
Cl^-	1.6×10^3	1.5×10^3	..

[a] At E of 0.1 N calomel electrode.

pseudo-rate constants, "constants" which depend on the concentrations of these other ions.)

A comparison of $\sqrt{k_{ex}/10^{11}}$ and $k_{el}/10^4$ on the basis of the existing experimental data is given in Table I. All rate constants are pseudo-rate constants, their use being justified under the conditions cited.[9] The qualitative trend in both k_{el} and k_{ex} is seen to be the same, and the values in the two columns are relatively close to each other, considering the fact that approximations in the theory enter exponentially (a fairer comparison would be of $\Delta F_{ex}^*/2$ and ΔF_{el}^*), that stationary electrodes (and their adsorption problems) were usually necessary, and that the work terms may not have been negligible. Other reactions for which the data are more fragmentary are described in Appendix II.

Comparison of Chemical and Electrochemical Oxidation–Reduction Rates of a Series of Related Reactants.—In this comparison we shall consider systems in which a constant reagent is used in the chemical system, and a constant electrode potential in the electrochemical one, to oxidize or reduce a series of related compounds. In a series of a given charge type, the work terms are either exactly or roughly constant in each of these two systems. Furthermore, if the ΔF^*'s are in the region where they would depend linearly on ΔF^0, then according to eq. 1 and 7 to 9 the ratio k_{soln}/k_{el} should be the same for each member of the series: In both cases, the terms λ_1, ΔF^0, and, at a constant E, η $(=E - E^0)$ will normally vary from member to member. (λ_2 refers to the constant reagent.) However, since ΔF^0 equals $(-nFE^0 + \text{constant})$ in the series, one sees from eq. 7 to 9 that these variations in λ_1, ΔF^0, and E^0 cancel when one compares values of $(\Delta F_{soln}^* - \Delta F_{el}^*)$, that is of k_{soln}/k_{el}. Vlcek[12] has recently observed that the electroreduction and the $Cr(dipy)_3^{+2}$ reduction[13] of $Co(NH_3)_6^{+3}$ and $Co(NH_3)_5(H_2O)^{+3}$ had essentially the same k_{soln}/k_{el} for both Co compounds (see Table II). This experimental result is in agreement with the above theoretical deduction. Presumably both E^0 and λ_1 differed in the two compounds. Extension of these comparative studies to other Co compounds would of course be desirable.

Similarly, the ratio k^a_{soln}/k^b_{soln} for each member of the series oxidized or reduced by two reagents, a and b, should be constant. This result was found experimentally for the $Co(NH_3)_5X$ (III) compounds reduced by $V(H_2O)_6^{+2}$ and $Cr(dipy)_3^{+3}$, respectively, with X being NH_3, H_2O, and Cl^-[14,15] (Table II). The restriction to a given charge type will not be important if the work terms are relatively minor. The comparison involving V^{+2} should be accepted with some reserve since the V(II) reaction is not necessarily an "outer sphere" one, as Taube has pointed out.

Salt and Solvent Effects.—The above comparisons suggest that some of the interesting phenomena observed in isotopic exchange reactions should be looked for in the corresponding electrochemical ones. For example, traces of Cl^- inhibit Tl(I)–Tl(III) isotopic exchange but greater amounts catalyze it.[16] Again, substitution of water by isopropyl alcohol decreased the rate of Fe(II)–Fe(III) exchange 10^8-fold.[17] This factor could be due to the enhanced coulombic repul-

mn pair, *i.e.*, if $|\Delta F_{mn}^{0xy}/(\Delta F_{mn}^{*xy})_0| \leqslant 1$. If any of these complexes decomposes in less than a vibrational period, ΔF_{mn}^{0xy} is to be computed for a "frozen" value of the unstable coördinate, the same value for both sides of the above equilibrium. There is some possibility that for certain deductions these conditions can be relaxed, a point which we shall investigate further.

(10) P. King, C. F. Deck and A. C. Wahl, 139th American Chemical Society National Meeting, 1961, Abstracts, p. 30R, and private communication. The value in Table I is a long extrapolation which was made using their equation describing data in the 0.0025 to 0.05 M KCl region. At 0.05 M KCl and corrected to 25°, $\sqrt{k_{ex}/10^{11}}$ was 1.6×10^{-4}.

(11) Z. Galus and R. N. Adams, Paper presented at the "Symposium on Mechanisms of Electrode Reactions," 142nd American Chemical Society National Meeting (1962). These authors found that in a variety of electrochemical reactions k_{el} averaged about 20-fold less for a carbon paste electrode than it did for a platinum one. Accordingly, their k_{el} for $MnO_4^{-1,-2}$ (0.01 cm. sec.$^{-1}$), which was obtained with carbon paste, was increased by a factor of twenty to obtain the value cited in Table I, so as to permit its comparison with the other systems.

(12) A. A. Vlcek, in "Sixth International Conference on Coördination Chemistry," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 590.

(13) A. M. Zwickel and H. Taube, *Discussions Faraday Soc.*, **29**, 42, (1960).

(14) A. M. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).

(15) Condition (10) is fulfilled for the V^{+2}–$Co(NH_3)_6^{+3}$ reaction, since $\Delta F^0 = -8$ kcal. mole^{-1}, $\Delta F^* = 18$ kcal. mole^{-1} whence $(\Delta F^*)_0 \sim (18 + 8/2)$ and $|\Delta F^0/(\Delta F^*)_0| \sim 1/3$. An E^0 or $E_{1/2}$ for $Cr(dipy)_3^{+2,+3}$ could not be found, so that condition (10) was not checked for the $Cr(dipy)_3^{+2}$–$Co(NH_3)_6^{+3}$ reaction. In the electrochemical reduction of $Co(NH_3)_5X$ (III), most of the transfer coefficients were near 0.5, though that for X = NH_3 was apparently 0.67.

(16) G. Harbottle and R. W. Dodson, *J. Am. Chem. Soc.*, **73**, 2442 (1951). For other references to anions which inhibit Tl(I)–Tl(III) exchange, see N. Sutin, ref. 3a.

(17) N. Sutin, *J. Phys. Chem.*, **64**, 1766 (1960).

sion. If not, the electrochemical exchange current may be reduced 10^4-fold.

Sutin has suggested[18] that it would also be interesting to study the electro-reduction of $Co(NH_3)_5X$ (III) when X is a fumarate methyl or phenyl ester, to see whether this reduction resembles more closely a reduction by $Cr(dipy)_3^{+2}$ or by V^{+2}. Hydrolysis of the ester accompanies the reduction in the second case but not in the first.

Cross-Reaction Rate Constants.—It follows from eq. 1, 7, and 9 that when condition (10) is fulfilled the forward rate constant k_{12} of the cross-reaction (11)

$$\mathrm{Ox}_1 + \mathrm{Red}_2 = \mathrm{Red}_1 + \mathrm{Ox}_2 \qquad (11)$$

is given by (12).

$$k_{12} \cong \sqrt{k_{11}k_{22}K_{12}}\,e^{-(w_{12} + w_{12}^{\mathrm{p}} - w_{11} - w_{22})/2RT} \qquad (12)$$

where k_{11} and k_{22} are the isotopic exchange rate constants in systems 1 and 2, w_{11} and w_{22} are the corresponding work terms, and K_{12} and w_{12}, w^{p}_{12} denote the equilibrium constant and the work terms of (11).

Equation 12 was derived earlier[5d] under a more eestrictive assumption ($k_j = k_j^{\mathrm{p}}$) and for negligible rxponent. Even if any or all of the species in (11) form weak complexes with other ions, (12) should still hold for the pseudo k's, provided (i) the conditions listed earlier[9] prevail, (ii) the coulombic contribution to $w_{12} + w^{\mathrm{p}}_{12} - w_{11} - w_{22}$ is negligible for each elementary electron transfer, and (iii) the non-coulombic one (see below) is either essentially the same for each pair or vanishes. When the coulombic term is not negligible, eq. 12 is to be used for each elementary electron transfer; if a participating complex is very unstable, K_{12} for this step is that computed when a coördinate is "frozen."[9]

For a somewhat more accurate comparison, k_{12} may be estimated from k_{11} and k_{22} using the complete equations 1 to 3, noting that $\lambda_{12} = (\lambda_{11} + \lambda_{22})/2$. (However, the generalization to weak complexes has not been established for the case where condition (10) does not hold.) When the work terms are negligible, eq. 1 to 3 yield

$$k_{12} = \sqrt{k_{11}k_{22}K_{12}f} \qquad (13)$$

where

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

When reaction 11 is one in which the reactants are aquo ions which interchange charges, one would expect $w_{12} = w^{\mathrm{p}}_{12} = w_{11} = w_{22}$. The work term in (12) then vanishes. On the other hand, when (11) is a reaction between an ion with hydrogen bonding ligands and one with organic ligands (*e.g.*, $Fe(H_2O)_6^{+2}$ + $Fe(phen)_3^{+3}$) one would expect that the non-coulombic contributions to the work terms will not cancel: w_{11} and w_{22} may have attractive non-coulombic contributions and (w_{12} + w_{12}^{p}) repulsive ones. In this event two deductions may be made: (i) k_{12} will be less than $\sqrt{k_{11}k_{22}K_{12}}$ and (ii) when suitable ratios k_{12}/k_{13} are taken, the non-coulombic contribution to the work term can essentially cancel in the ratio (*e.g.*, if k_{12} corresponds to the reaction of $Fe(phen)_3^{+3}$ or $^{+2}$ with $Fe(H_2O)_6^{+2}$ or $^{+3}$ and k_{13} corresponds to the reaction of $Fe(phen)_3^{+3}$ or $^{+2}$ with another aquo-ion).

(18) N. Sutin, private communication.

Deduction (i) may explain the results of a comparison[3a] of k_{12} and $\sqrt{k_{11}k_{22}K_{12}}$ for the Fe^{+2}–$Fe(phen)_3^{+3}$ system. A value of a few kcal. mole^{-1} for $(w_{12} + w_{12}^{\mathrm{p}} - w_{11} - w_{22})/2$ would suffice to explain the results. Deduction (ii) was suggested by a comparison of k_{12}/k_{13} with $\sqrt{k_{22}K_{12}/k_{33}K_{13}}$ made by N. Sutin.[18] A variety of experimental tests involving the cross-relations is now in progress by Sutin and collaborators.[18]

Often in the literature the role of ΔF^0 (and hence of K_{12}) has been ignored in explaining the values of certain rate constants. Equation 12 (or indeed eq. 1 to 3) illustrates how important it can be for the present class of reactions.

Ligand-Field Effects.—The influence of ligand-field effects on the rate constants of oxidation–reduction reactions and on other properties of complex ions has been the subject of much interest. They are incorporated in the present theory; in particular they influence k_j, Δq_j^0, and ΔF^0. Accordingly, the present approach converts discussions of ligand-field effects on kinetic problems into a discussion of the problem of estimating k_j, Δq_j^0, and ΔF^0. Moreover, according to eq. 1, 7, 8, and 9, these effects cancel when certain correlations of the experimental data are made: the correlations embodied in chemical and electrochemical transfer coefficients of 0.5, in the comparison of chemical and electrochemical exchange "currents," and in the comparison of cross and isotopic exchange rate constants.

One *vs.* Two-Electron Transfers.—In some reactions involving 2-electron oxidation–reduction reagents, it has not been possible to decide whether the mechanism proceeds *via* two successive one-electron transfers or *via* one two-electron transfers. However, it is sometimes possible to distinguish between the two alternative mechanisms in a corresponding electrochemical reaction. For example, the Tl(I)–Tl(III) electrochemical process has been found to proceed *via* two one-electron transfers.[8g] From the electrochemical rate constants for the Tl(I)–Tl(II) and Tl(III)–Tl(I) reactions, we have computed in Appendix I a rate constant which may be compared with the homogeneous rate constant. Agreement would be expected only if the homogeneous rate constant proceeds *via* two one-electron transfers. The agreement in Table I for this comparison would appear to favor this mechanism for the homogeneous reaction. Had the value for $\sqrt{k_{\mathrm{ex}}/10^{11}}$ been appreciably greater than that for $k_{\mathrm{el}}/10^4$ (or really appreciably more than 10-fold greater since the electrode was Pt rather than Hg) one would have obtained evidence for the one two-electron homogeneous reaction instead.

Concluding Remarks.—The above correlations offer a possible way of systematizing and comparing experimental data both on electrochemical and on chemical electron transfer reactions. Some of the isotopic exchanges discussed earlier may not involve electron transfer and could involve atom transfer instead. The extent of correlations such as those in Table I may eventually provide a test of the mechanism, at least in the cases of extreme discrepancy.

There are a variety of other reactions for which the experimental electrochemical and isotopic exchange rate constants could be compared, and of related reactions for which chemical and electrochemical transfer coefficients could be determined. Several recent detailed surveys of the literature[3,4] should be very helpful for this purpose. More frequent collaboration between electrochemists and chemical kineticists would be useful for this purpose.

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Appendix I

An Analysis of the Tl(I)–Tl(III) System.—In ref. 8g the following k values were estimated at the formal potential of Tl(I) = Tl(III) + 2e in 1 M $HClO_4$ at 25°

$$\mathrm{Tl(III)} \longrightarrow \mathrm{Tl(II)} - \mathrm{e} \qquad k_{32}^{\mathrm{el}} = 1 \times 10^{-5} \text{ cm. sec.}^{-1}$$

$$\mathrm{Tl(I)} \longrightarrow \mathrm{Tl(II)} + \mathrm{e} \qquad k_{12}^{\mathrm{el}} = 3.5 \times 10^{-3} \text{ cm. sec.}^{-1}$$

We shall designate λ by appropriate subscripts and let E_{ij}^0 be the formal half-cell potential (in 1 M $HClO_4$ at 25°) of Tl(i) = Tl(j) + $(j - i)$e $(j > i)$. Equations 1, 8, and 9 then yield, when the work terms are neglected

$$-RT \ln k_{32}^{\mathrm{el}}/Z^{\mathrm{el}} = \frac{\lambda_{23}^{\mathrm{el}}}{4} + \frac{F\eta_{32}}{2}, \ \eta_{32} = -\ (E^0_{13} - E^0_{23})$$

$$-RT \ln k_{12}^{\mathrm{el}}/Z^{\mathrm{el}} = \frac{\lambda_{12}^{\mathrm{el}}}{4} + \frac{F\eta_{12}}{2}, \ \eta_{12} = E^0_{13} - E^0_{12}$$

since the transfer coefficients are in fact 0.5,[8g] so eq. 9 applies, and since the k's were given at E^0_{13}, rather than at the unknown E^0_{23} or E^0_{12}.

Noting further that $(E^0_{23} - E^0_{12})F$ is ΔF^0, the "standard" free energy of reaction A1 in the prevailing medium

$$\mathrm{Tl(III)} + \mathrm{Tl(I)} = 2\mathrm{Tl(II)} \qquad \text{(A1)}$$

one obtains

$$-RT \ln k_{32}^{\mathrm{el}}\, k_{12}^{\mathrm{el}}/Z^{\mathrm{el}^2} = \frac{\lambda_{23}^{\mathrm{el}} + \lambda_{12}^{\mathrm{el}}}{4} + \frac{\Delta F^0}{2}$$

However, it can be shown from eq. 1, 7, and 8 that the forward rate constant of the homogeneous reaction (A1), k^{ex}, should be given by

$$-RT \ln k^{\mathrm{ex}}/Z^{\mathrm{soln}} = \frac{\lambda_{23}^{\mathrm{ex}} + \lambda_{12}^{\mathrm{ex}}}{8} + \frac{\Delta F^0}{2}$$

Since $\lambda^{\mathrm{ex}} \leqslant 2\ \lambda^{\mathrm{el}}$ it then follows that to test the theory $\sqrt{k^{\mathrm{ex}}/Z}$ should be compared with $\sqrt{k_{32}^{\mathrm{el}}k_{12}^{\mathrm{el}}}/Z$. For this reason the geometric mean of k_{32}^{el} and k_{12}^{el} was used in Table I.

Appendix II

Comparisons in Other Systems.—Fragmentary information exists about electrochemical and chemical exchange rates in a number of other systems.

$Co(NH_3)_6^{+2,+3}$.—Both the electrochemical and chemical rates are extremely small. The electrochemical reduction of $Co(NH_3)_6^{+3}$ in 0.14 M $HClO_4$ and 1.26 M $NaClO_4$ at 25° has a rate constant of 2.1×10^{-4} $\sqrt{D}$ cm. sec.$^{-1}$ when the formal applied potential E is 0 *vs.* 0.1 N calomel electrode[10] (D is the diffusion coefficient). Taking the formal E^0 for the $Co(NH_3)_6^{+2,+3}$ system to be[19] ~0.22 volt *vs.* 0.1 N calomel, the transfer coefficient to be 0.67,[12] and $D \sim 10^{-5}$ cm.^{2} sec.$^{-1}$, the value of $k_{\mathrm{el}}/10^4$ at $\eta_a = 0$ is found to be 2×10^{-12}. If a transfer coefficient of 0.5 had been used, the value would have been 9×10^{-12}.

From isotopic exchange rate constants and equilibrium constants obtained at 65°,[20] one may estimate that $\sqrt{k^{\mathrm{ex}}/10^{11}} < 5 \times 10^{-11}$ in 0.14 M H^+ at 65°. Presumably, therefore, $\sqrt{k^{\mathrm{ex}}/10^{11}} << 5 \times 10^{-11}$ at 25°, a result consistent with the above value of $k^{\mathrm{el}}/10^4$.

Ce(III)–Ce(IV).—The value of $k_{\mathrm{el}}/10^4$ for this system in 1 N H_2SO_4 at 25° is 8b $\sim 10^{-8}$. Unfortunately, the electrochemical transfer coefficient for oxidation was apparently 0.75, a value so different from 0.5 that a comparison with the exchange data can be questioned. (The magnitude of the chemical transfer coefficient for the Ce(IV)–$Fe(phen)_3^{+2}$ system is of particular interest and is under current investigation.[18]) The value of $\sqrt{k_{\mathrm{ex}}/10^{11}}$ is 7×10^{-6} in 0.8 N H_2SO_4 at 25°.[21]

Cr(II)–Cr(III).—The electrochemical exchange current for this system has been measured at 20° in 1 M KCl where hydrolysis is presumably appreciable.[22] The value of $k_{\mathrm{el}}/10^4$ is 1.0×10^{-9}. From the isotopic exchange rate data[23] at the lowest acid concentration studied (0.2 M $HClO_4$, 0.8 M $NaClO_4$), one may estimate $\sqrt{k_{\mathrm{ex}}/10^{11}} = 5 \times 10^{-7}$ at 20°.

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