

9. R. A. Marcus (to be submitted). 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° 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 coordinate at the intersection surface of Ref. 5e, though it can occur before or later.

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 $A X_m + B Y_n \rightleftharpoons A^P X_m + B^P Y_n$, ΔF_{mn}^{oxy} , satisfies condition (10) for every important mn pair, i.e. if $|\Delta F_{mn}^{oxy} / (\Delta F_{mn}^{oxy})_0| \leq 2$. If any of these complexes decomposes in less than a vibrational period, ΔF_{mn}^{oxy} is to be computed for a "frozen" value of the unstable coordinate, the same value for both sides of the above equilibrium. There is some possibility that for certain deductions conditions (i) and (iii) can be relaxed, a point which we shall investigate further.

10. P. King, C.F. Deck and A.C.Wahl, 139th A.C.S. National Meeting, (1961), Abstracts, p. 30 R, and private communication. The value in Table I is a long extrapolation which I 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°C, $\sqrt{k_{ex}}/10^{11}$ was 1.6×10^{-4} .
11. Z. Galus and R. N. Adams, Paper presented at the "Symposium on Mechanisms of Electrode Reactions," 142nd A.C.S. 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 $MnO_4^{-1,-2}$ ($0.01 \text{ cm sec.}^{-1}$), 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 Coordination Chemistry", S. Kirschner, Ed., Macmillan, New York (1961), p. 590.