

ELECTRON TRANSFERS AT ELECTRODES AND IN SOLUTION.
COMPARISON OF THEORY AND EXPERIMENT

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Detailed quantitative information about different theoretical aspects of electron transfer rates in solution and at electrodes can be obtained from appropriate experiments. Recent theoretical work has predicted certain quantitative correlations between rates of crossed-redox reactions and rates of isotopic exchange, and between homogeneous and electrochemical rates. Experimental tests of these predictions yield insight into "intrinsic" and "driving force" factors.

The intrinsic factor is related to differences in properties of oxidized and reduced species (e.g., differences in corresponding bond lengths and differences in solvent orientation polarization). The driving force term is related to the standard free energy of reaction in the homogeneous reaction and to the activation overpotential in the electrode reaction.

Measurements of temperature coefficients of rates in dilute solution provide some information about adiabatic and dielectric saturation effects. Absolute rates, in conjunction with knowledge of bond length differences and bond force constants, provide some insight into the overall picture, though do not disentangle these various factors (intrinsic, adiabatic, unsaturation, etc.).

The present state of experimental information on these theoretical topics will be described.