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Reflections on electron transfer theory F

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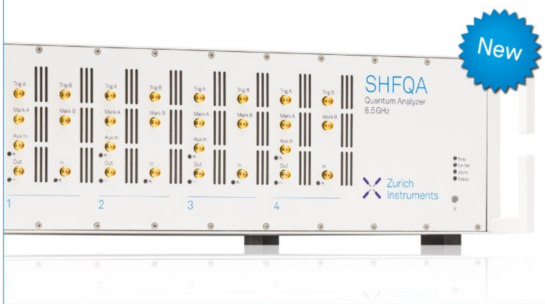

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Some of the early history leading to the 1956 *The Journal of Chemical Physics* article on a theory of electron transfer reactions is described.

In the development of electron transfer theory in 1956,[1] the simplicity of the final equation for the free energy barrier, after a lengthy and complex derivation, came to me as a surprise. It was indeed a "Eureka" moment, and I give some of its history here.

The theory developed via a rather circuitous route, beginning with a question from a graduate student in a class on statistical mechanics that I taught at Brooklyn Poly. The question was whether a certain model (the Ising model) involving nearest neighbor interactions could be applied to shielded charges along a polymeric chain, a polyelectrolyte. His interest was in applying the theory to experimental data he was obtaining in the laboratory. The answer was yes, and I became interested more generally in the electrostatic properties of polyelectrolytes and in the several seemingly different ways of calculating their electrostatic free energy.

To extend my background in electrostatics and treat this topic in a more fundamental way I researched every book on electrostatics/electromagnetic theory in the Brooklyn Poly library and found one[2] that provided physical insight into the various concepts. After writing a pair of articles on polyelectrolytes, I then wondered what to do next. I had long decided that applying a theory I derived in 1952, later known as Rice–Ramsperger–Kassel–Marcus (RRKM) theory, was not a desirable option. There were almost no relevant experimental data on unimolecular reactions or bimolecular recombination reactions at the time. Extensive data, laboratory and computational, for testing the theory were to come later in the 1960s and subsequent decades.

Still uncertain on what to do, I came across in the library a symposium on radiation chemistry published in 1952 in the Journal of Physical Chemistry. The symposium was organized by Professor Milton Burton of the University of Notre Dame Radiation Lab. It happened that Burton, a friend of my post-doctoral mentor O. K. Rice at the University of North Carolina, had suggested to Rice that I present a paper on my recent work on the theory of $CH_3 + I \rightarrow CH_3I$ recombination at a forthcoming 1950 symposium "Anomalies in Reaction Kinetics" at the University of Minnesota. Whether or not it was due to that association I read the various articles in the Burton symposium and was especially intrigued by an article by Libby.[3]

Libby applied the Franck–Condon principle to explain why some isotopic exchange electron transfer reactions were fast and others slow, the reaction rate depending on the radius of the ions involved. The connection with radiation chemistry was that these studies used radioactive isotopes as tracers of the course of the reactions and reflected the general interest in atomic energy related topics at the time. Libby pointed out that when an electron is transferred from one ion or molecule to another, the "jump" is instantaneous and the nuclear environment around each ion does not have time to change during the jump itself (the Franck–Condon principle). In this case, the system now has a much higher energy than before the jump, since the new charges are now in unequilibrated environments. The smaller the ions, the larger the ionic electric fields involved and the larger the increase in the post-jump energy and so the higher the energy barrier to the reaction.

This application of the Franck–Condon principle to a chemical reaction was heady material, and I was excited in learning more about this new topic. It was certainly not the language seen in theories of conventional chemical reaction rates. However, as I began to think further about it, I became uneasy; some aspect did not seem right. Yes, the nuclei did not have time to move during an electron jump from one reactant to a neighboring reactant, and yes, the energy of the system after the jump would be greater than before, and the effect would be the greater the smaller the ionic radii. I then realized that what was missing was the source of this extra energy of the reaction products. As great as the idea of applying the Franck–Condon principle was, its application in this way violated the law of conservation of energy. The answer had to be in some rearrangement of the dielectric polarization around the ions

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prior to the electron transfer, so that the system had to pass through a non-equilibrium configuration of the dielectric polarization, with the constraint that when the electron transfer actually occurs there is a conservation of total energy.

Hence, the problem became one of expressing the free energy of the reactants and their environment in terms of a non-equilibrium dielectric polarization function everywhere in the medium and finding that unknown polarization function. With the background I had developed reading Mason and Weaver, and also with reading the related material in physics on polaron theory, I was able to derive an expression for the total free energy of the system containing a nonequilibrium dielectric polarization, taking into account the different responses of the various parts, fast and slow, of the dielectric polarization. The minimization of the free energy subject to the constraint that the free energy does not change during the electron jump (neither the energy nor the configurational entropy of the system change) led to a variational problem for the unknown non-equilibrium dielectric polarization function in the transition state. The solution of the problem led to finding that dielectric function and with it an expression for the free energy of activation of the electron transfer reaction. At an intermediate step, the expression was unusually complex, but application of a theorem on integrals led to the simple expression used today.

This electron transfer field has been rich in the variety of new experiments, experiments that have stimulated theory, and theory that has stimulated new experiments. It has been a long step from a graduate student's question on polyelectrolytes to modern electron transfer theory, but the steps were taken nevertheless.

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