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OBITUARY

Theory as a lighthouse in the electrochemical ocean

In memory of Alexander M. Kuznetsov

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Professor Alexander M. Kuznetsov, a world-recognized theoretician, passed away on February 12, 2009 in Moscow. Until his last days, he continued to work on various aspects of charge transfer phenomena. All his scientific life, starting from early 1960s, was devoted to this enormous and intriguing research field. He deeply penetrated into important details of charge transfer in physics, chemistry, and biology (this is just the title of his well-known book [1], later continued jointly with Jens Ulstrup [2]). Heterogeneous charge transfer in electrochemical systems was at the heart of this activity.

Usually, in electrochemistry, one meets many obstacles (both in modeling and also psychologically) when constructing links between theory and experimental facts. The main reason is the obvious complexity of an electrified interface formed by two condensed phases of essentially different structure, with strongly inhomogeneous charge distribution. Moreover, experimental electrochemists are able to extract any information about electron transfer only by changing the potential (charge) at this interface, i.e., all events under consideration take place in a very specific area of variable state. The latter is crucial for theory parameters, which can be estimated (even roughly) only by modeling the interfacial "reaction layer."

In electrochemical kinetics, the theory always outruns the experiment, and the quantum mechanical theory of charge transfer created in the famous Theoretical Department of the Frumkin Institute in Moscow (R.R. Dogonadze, A.M. Kuznetsov, and co-authors) is a good example for that. The same takes place now with recent advancements in the theory of electron transfer in configuration of scanning tunneling microscope (A.M. Kuznetsov, J. Ulstrup, and I.G. Medvedev). Although Alexander Mikhailovich sadly had only a short time to see some experimental confirmations of his predictions for single molecule behavior in STM, his name remains known in this modern high-tech oriented area, a branch of molecular electronics.

Alexander Mikhailovich Kuznetsov was a person who inspired us, individually and as a team, to follow a long and interesting experiment-modeling-theory route. His unique skill was the ability to grasp immediately the essence of any particular or general problem and to show key links between the problems. With the same rapidity, he extracted important references from his bright memory, outlined research plans, and made quantitative estimates. Due to his profound knowledge and intuition, he kept us several times away from mistakes which could have led to a wrong interpretation of intermediate results. However, the most essential point was his fast and friendly reaction in any discussion.

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Being a brilliant theoretician, Alexander Mikhailovich always demonstrated a vivid interest both in challenging experimental data and (during the last decade) to computational electrochemistry. It should be stressed that modern charge transfer theories play a first fiddle in molecular modeling, as without theoretical background even very sophisticated calculations resemble routine chemical combinatorics. Only the interplay between theory and computer simulations favors the development of really interesting and useful microscopic models.

Two milestones of our long contacts are related to various reaction free energy surfaces (asymmetry of intramolecular reorganization and bond breaking electron transfer). This is the case when theoretical predictions can explain many deviations of experimental current–voltage curves from Tafel-like behavior, although the application of theory is less transparent. Another long and exciting story is the recognition of activationless electron transfer in the well-known current–voltage curves of anions electroreduction at high overvoltage. Surprisingly, theoretical results necessary for this explanation were available from the works of Dogonadze and Kuznetsov published already in the 1960s (see [1–6] for reviews), i.e., in the same time when early experimental data already appeared. The key physical effect of the transfer coefficient decrease was masked, however, by strong electrostatic repulsion, and traditional interpretation (never quantitative and rather uncertain) was constricted to double-layer effects.

Together with A.M. Kuznetsov, we combined the theory with Monte Carlo simulations to explore heterogeneous electron transfer using a network formed by crossing free energy surfaces which model a manifold of electronic states in a metal electrode. Jointly, we also succeeded to describe the stepwise electroreduction of Zn(II) from aqueous solution by means of quantum chemical calculations and adiabatic electron transfer theory. We remember how patiently he explained to us some pitfalls in using the Anderson model Hamiltonian. It was a great pleasure to collaborate with him in the quantum chemical modeling of the discharge of a hydronium ion at the mercury electrode, where just the Dogonadge–Kuznetsov–Levich theory was successfully employed. This challenging reaction attracted our attention for many years, and the microscopic modeling finally confirmed the earlier theoretical conclusion about proton transfer from exited energy levels as a key effect leading to the famous Tafel plot in a wide overvoltage region.

Being always versed in new theoretical approaches, A.M. Kuznetsov wrote an excellent book on stochastical theory of charge transfer in liquids [7] which, together with Zusman's works, pioneered a broad model treatment of multifarious solvent dynamics effects in interfacial electrochemistry. We greatly appreciate very fruitful discussions with Alexander Mikhailovich on different aspects of solvent dynamics problems from theoretical and computational viewpoints.

"Time moves like an arrow," says an old Chinese proverb. The advent of new experimental methods, more perfect devices, and powerful computers makes it possible very soon to gain a deeper insight into unsolved problems of electrochemical kinetics, and we will have probably to revisit many old results and concepts. Nevertheless, the A.M. Kuznetsov ideas and theoretical findings will be certainly employed for a long time and facilitate for many people their rambling in the complicated but fantastically interesting world of charge transfer phenomena.

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