This Week's Citation Classic

Koutecký J. Theory of slow electrode reactions in the polarography and polarographic behaviour of a system in which the depolarizer is generated with a rapid chemical reaction from an electroinactive compound.
Collect. Czech. Chem. Commun. **18**:597-610, 1953.
[Lab. Physical Chemistry, Czechoslovak Acad. Sci., Prague, Czechoslovakia]

A general formulation both for slow electrode reactions at the dropping mercury electrode and for kinetic polarographic currents was found and the solution derived with the help of dimensionless quantities. The interpolation formula for average kinetic polarographic currents is in agreement with experimentally found dependences on relevant parameters, and it has a form very similar to the older approximate equations of Brdička and Wiesner.[1] [The *SCI*® indicates that this paper has been cited over 375 times since 1961.]

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March 17, 1982

"My fellow students in chemistry at the university in Prague had called my attention in 1947 to a problem in electrochemistry which looked interesting to them. According to Rudolf Brdička,[2,3] polarographic kinetic currents are caused by fast recombination of organic acids in the immediate neighbourhood of the electrode. A theory could, therefore, have been used for determination of rates of very fast reactions, but an appropriate theory did not exist.

"At that time I was at Charles University in Prague trying as quickly as possible to make up for the delay in my education in theoretical physics caused by the closing of the Czech universities by the Nazis during World War II, and I considered this excursion into physical chemistry an interesting diversion only. With Brdička I attacked this problem by solving the differential equations for kinetic polarographic currents without paying attention to the hydrodynamical consequences of the growing mercury dropping electrode.[4] The resulting 'exact' theory was in worse agreement with the experiments than the very rough approximate theory of Brdička and Wiesner.[1]

"This failure of the mathematical formulation was bewildering to me and therefore, after I was not allowed to continue my university studies following the communist takeover in 1948, I tackled this problem, this time privately as an 'additional occupation.' In 1951, it became clear to me that the hydrodynamics must be considered in the differential equations simultaneously with the diffusion and the chemical reaction. In a series of papers the problem of kinetic currents was solved with a sufficient precision for the experimental purposes of that time.

"In 1954, five years after my stay in a forced labour camp, I was awarded jointly with Brdička the state prize, which in Czechoslovakia is considered a very prestigious honour, for the discovery and solution of polarographic kinetic currents. Due to Brdička's insistence on sharing the prize with me, my return to scientific activity was possible. Because of difficult circumstances which existed in many European countries after World War II, the merits of generous scientists with personal integrity and civil courage such as Brdička cannot be emphasized enough.

"I believe that this paper is so frequently quoted because the polarographic currents provide a possibility to estimate the velocity of very fast chemical reactions with very simple experimental means. A complicated phenomenon was simplified with help of transparent and physically well-defined concepts, which made possible the exact mathematical solution of the problem. In addition this solution was approximated with a closed form interpolation formula suitable for evaluation of experimental results. D.D. Macdonald has recently published work in this field."[5]

1. **Brdička R & Wiesner K.** Rate of recombination of ions derived from polarographic limiting currents due to the reduction of acids. *Collect. Czech. Chem. Commun.* **12**:138-49, 1947.
2. **Brdička R.** Polarographic investigation of tautomeric equilibriums. *Chem. Listy* **39**:35-47, 1945.
3. ----------, The mechanism of the polarographic reduction of pyruvic and phenylglyoxylic acid. *Collect. Czech. Chem. Commun.* **12**:212-35, 1947.
4. **Koutecký J & Brdička R.** Fundamental equation for the electrolytic current when depending on the formation rate of the depolarizer jointly with diffusion and its polarographic verification. *Collect. Czech. Chem. Commun.* **12**:337-55, 1947.
5. **Macdonald D D.** *Transient techniques in electrochemistry.* New York: Plenum, 1977. 329 p.