

## Wagner-Traud to Stern-Geary; Development of Corrosion Kinetics

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In 1938, Wagner and Traud published the paper that underlies all of the electrochemical kinetics for corrosion. They elegantly put forth the concepts of local anodes and cathodes operating at a mixed potential. They also showed that the rate of redox reactions at a mixed electrode could be determined by extrapolation of the linear portions of the polarization curve drawn on a semilog plot, and also that it could be approximated from the slope of the current potential curve. Many consider that the next major contribution to the field of corrosion kinetics was made by Stern in a series of papers from 1955-57. Those papers show how measured polarization curves represent a summation of the kinetics for the individual electrochemical reactions. The 1957 Stern and Geary paper proves that corrosion rate is inversely proportional to the slope of the measured polarization curve at the corrosion potential, an expression that has come to be known as the Stern-Geary equation. The last 2 sentences of the Stern-Geary paper admit that the findings are consistent with those of Wagner and Traud from almost 20 years earlier. In fact, the Wagner-Traud paper had developed an equivalent expression. Many papers published during the intervening papers had shown that this relationship existed experimentally, but were apparently not aware of Wagner-Traud, which was published in German. This review will examine these contributions and investigate why it took so long to advance from Wagner-Traud to Stern-Geary. The social and scientific upheaval associated with WWII certainly contributed to this gap in time.

Another issue will also be addressed in this paper. All computer-automated potentiostats now provide analysis packages for determining corrosion rate and Tafel slopes from potentiodynamic polarization curves by non-linear least squares fitting of the data to an equation. This equation is a sum of two exponentials, and describes the expected measured polarization curve for a corroding system in which a single anodic reaction and a single cathodic reaction both exhibit perfect activation-controlled kinetics. The equation is identical in form to the measured polarization curve around the reversible potential for an electrochemical half-reaction in equilibrium, which is called the Butler-Volmer equation. This Butler-Volmer-like equation at the corrosion potential has no name by which it is commonly referred, and it is not clear who should get credit for it. Wagner and Traud came very close to writing it out, but did not do so explicitly. Neither did Stern. From the Wagner-Traud paper, however, it is clear that they understood the underlying concepts. They obviously did not have the means to make use of such an equation by non-linear least squares fitting of the data. In light of the contribution that their paper made to the field, and the fact that they came very

close to deriving this equation, it is proposed that the equation be known as the Wagner-Traud equation.