

Trasatti S. Work function, electronegativity, and electrochemical behaviour of metals.

II. Potentials of zero charge and "electrochemical" work functions.

*J. Electroanal. Chem.* 33:351-78, 1971.

[Laboratory of Electrochemistry, University of Milan, Italy]

Electron work functions, electronegativity, and potentials of zero charge of metals are shown to be linearly interrelated. Metals gather into different groups. The differences between groups and within a group along a series of metals are explained in terms of chemical interactions between the phases governed by the electronegativity of the metal surface. [The *SCI*® indicates that this paper has been cited in over 200 publications.]

Sergio Trasatti  
Department of Physical Chemistry and  
Electrochemistry  
University of Milan  
20133 Milan  
Italy

June 20, 1987

This paper marked a milestone in my scientific career. Soon after its publication I received, through the journal's editor, a letter from the Olympus of electrochemists: A.N. Frumkin of the Academy of Sciences of the USSR. He was interested in my work, and the letter initiated an exciting (at least for me) exchange of letters that was stopped only by his unfortunate death in 1976. Almost at the same time I received my first international invitation for a lecture and the first commitment for a chapter in a book.

The paper was the second of a series of four I published between 1971 and 1973 on the relationship between the electronic structure of metals and their electrochemical behaviour. I had long been intrigued by the structural and electronic factors that can be responsible for the electrochemical behaviour of metals as a result of my own research in electrochemistry and by having taught metals science since 1963. I had always been convinced that nature is orderly and regular, and I had often wondered whether it would be possible to arrange the metals by specific properties in a regular sequence that could be useful for interpolations and extrapolations. The energy of the electrons at the Fermi level, known as the work function, turned out to be such a property.<sup>1</sup>

The difference between the behaviour of metals in a vacuum and of metals in a solution (as electrodes) had been of interest since the pioneering work of Frumkin in the 1920s. However, the proposed correlations were always rather featureless

and nonilluminating since they showed that the difference was a constant irrespective of the nature of the metal. I felt that this outcome could be due to an insensitive analysis of the existing work function data, so I started with a critical search in the literature. The first paper<sup>2</sup> of the series resulted from this search.

I moved then to the thermodynamically predictable relationship between the work function and the potential of zero charge that corresponds to the electrochemically measured relative electronic energy of a metal. As I plotted the two quantities against each other, I was excited to see that metals gathered into different groups that were closely related to their position on the periodic table so that the behaviour of each metal could ultimately be related to the classic concept of electronegativity.

In my opinion the main reason for the impact of this paper on the scientific community was that it suddenly enlarged the horizon of the possible interpretations of the structure of an electrochemical interface. The reason for Frumkin's interest was that the rationalization was possible because of the wealth of experimental data from his school. He had already placed the seed by comparing the experimental behaviour of Ga and Hg, two metals at the extremes of the activity scale (a fact I have acknowledged elsewhere<sup>3</sup>). I did not discover a new relationship; I simply threw light on its actual form by making a critical evaluation of the data then available. I was certainly not the first to attempt such correlations. I was probably a bit more selective, and I attached importance to some systematic deviations from an average picture that others had either neglected or overlooked.

Even though more refined experimental data later allowed more precise location of a few metals in the correlations, the general picture has never been disproved. It has also in fact been supported by theoretical approaches,<sup>4</sup> even though the physical interpretation of the correlations has evolved somewhat to emphasize the role of the electron distribution at the metal surface, which in the original paper was assumed to be constant as a first approximation.<sup>5</sup> However, in my opinion, in spite of its semiempirical approach, the paper marked a decisive turn in electrochemistry from the traditional purely electrostatic to the modern physicochemical description of the structure of the region between a metal electrode and a solution. For this reason it became a *Classic*.

My paper was the result of a period of intense meditation, and consequently my scientific life has become so intense that I now have much less time for thinking. This probably constitutes a typical contradiction of life.

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3. ———. Solvent adsorption and double layer potential drop at electrodes. (Conway B E & Bockris J O, eds.) *Modern aspects of electrochemistry*. New York: Plenum Press, 1979. Vol. 13. p. 81-206. (Cited 55 times.)
4. Badiali J P, Rosinberg M L & Goodisman J. Effect of solvent on properties of the liquid metal surface. *J. Electroanal. Chem.* 130:31-45, 1981.
5. Trasatti S. Potentials of zero charge. What they suggest about the structure of the interfacial region. (Silva A F, ed.) *Trends in interfacial electrochemistry*. Dordrecht, The Netherlands: Reidel, 1986. p. 25-48.