

Stumm W, Huang C P & Jenkins S R. Specific chemical interaction affecting the stability of dispersed systems. *Croat. Chem. Acta* 42:223-45, 1970. [Lab. Applied Chem., Harvard Univ., Cambridge, MA]; and **Stumm W, Kummert R & Sigg L.** A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide interfaces. *Croat. Chem. Acta* 53:291-312, 1980. [Swiss Federal Inst. Technol., Inst. Aquatic Sci., Zurich, Switzerland]

It was shown that H^+ and cations (metal ions) can interact chemically with hydrous oxide surfaces. To assess colloid stability, it is necessary to consider chemical forces in addition to those of the electric double layer. [The *SCI*[®] indicates that these papers have been cited in over 105 and 110 publications, respectively, making them the two most-cited papers from this journal.]

Coordination Chemistry at the Solid Water Interface

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The senior author—at the time a professor of applied chemistry at Harvard University—presented this paper in 1969 at the first International Summer School on the Chemistry of Solid-Liquid Interfaces organized by the Ruder Boskovic Institute of Zagreb under the leadership of the late Bozo Tezak and Velimir Pravdic. The coauthors were PhD students: C.P. Huang is now a professor at the University of Delaware, and S.R. Jenkins is a professor at Auburn University. I enjoyed the stimulating interaction with an international group of electrochemists and surface scientists at this summer school so much that I have returned to all subsequent seven conferences; and the proceedings that we prepared, always together with some doctoral students or junior collaborators for each one of these summer schools, read like a “continuation novel” of our research and our understanding of the coordination chemical model of the interaction of mineral surfaces with H^+ , OH^- , metal ions, and ligands.^{1,2}

For the past decades, the electric double layer model was the conceptual framework to interpret many surface chemical phenomena. But we pointed out in this paper that the chemical interactions of solutes with natural surfaces has to be considered in addition to those of the electric double layer. While the surface in the electric double layer model is assumed to be a structureless continuum (like an electrode), the basic concept in the surface functional groups, e.g., OH -groups, formed on all natural inorganic and organic hydrous solids. These functional groups contain the same donor atoms as found in functional groups of many soluble ligands and thus interact coordinatively with protons and metal ions. A most significant advance was made by Laura Sigg³ of the Institute for Water Resources and Water Pollution Control, who showed that the concept could be extended to the interaction of hydrous metal oxides with ligands, i.e., the metal ions in the surface layer of the oxide—acting as Lewis acids—can replace their coordinated OH -groups by ligand exchange reactions with anions or weak acids. She also showed⁴ by linear free energy relations that the tendency to form (inner-sphere) complexes in solution can be correlated to the tendency to form corresponding surface complexes.

A concerted effort of three of my PhD students, G. Furrer,¹ B. Wehrli,² and E. Wieland,² was very successful in demonstrating the applicability of the surface complex formation model to surface reactivity. They derived—by considering surface coordination, lattice statistics, and activated complex theory—a unifying kinetic law for the surface controlled reactions such as dissolution (and weathering of minerals) to surface catalyzed redox reactions and to many photocatalytic surfaces. The newest developments on the dependence of surface reactivity on surface structure are reviewed in a recent contribution to *Croatica Chemica Acta*.⁴ That surface complexation has come of age is demonstrated by two recent books.^{5,6}

In all our work we were stimulated by the contributions of Paul Schindler (University of Bern), James Morgan (California Institute of Technology), François Morel (Massachusetts Institute of Technology), Charles O'Melia (Johns Hopkins University), and Garrison Spotia (University of California, Berkeley).

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3. Sigg L & Stumm W. The interaction of anions and weak acids with the hydrous goethite (α -FeOOH) surface. *Colloid. Surface* 2:101-17, 1981. (Cited 90 times.)
4. Stumm W, Sulzberger B & Stumm J. *Croat. Chem. Acta* (In press.)
5. Stumm W, ed. *Aquatic surface chemistry; chemical processes at the particle-water interface*. New York: Wiley-Interscience, 1987. 520 p.
6. Dzombak D A & Morel F M M. *Surface complexation modeling*. New York: Wiley-Interscience, 1990. 393 p.