

Bunnett J F. Kinetics of reactions in moderately concentrated aqueous acids.

1. Classification of reactions. *J. Amer. Chem. Soc.* **83**:4956-67, 1961.

Plots of  $(\log k_{\psi} + H_{\psi})$  or other appropriate function against  $\log a_{H_2O}$  are generally linear or approximately so. The slopes define a parameter,  $w$ , which is recommended for the precise classification of reactions.  $w$  values show no particular tendency to cluster about magnitudes corresponding to the ideal' Zucker-Hammett categories. Classification according to the ZuckerHammett categories requires arbitrary decisions in some cases and in general obscures subtle and important differences. [The SC<sup>®</sup> indicates that this paper has been cited 344 times since 1961.]

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"Perhaps the reason this paper was cited rather often is that, in the terminology of T S Kuhn,<sup>1</sup> it successfully challenged the thenprevailing paradigm in its field.

"The paper was concerned with quantitative treatment of the rates of chemical reactions in mineral acid solutions, mainly in sulfuric acid. It was known that reaction rate depended on the acid concentration, but that the magnitude and even the direction of dependence varied from one reaction to another.

"The great pioneer investigator in this area was Louis P. Hammett In 1939 he proposed an hypothesis to the effect that the kinetic behavior of reactions in mineral acid solutions falls into one or the other of two tightly defined categories, with each of which a characteristic type of reaction mechanism was associated In part because of Hammett's eminence, the Zucker-

Hammett hypothesis (as it came to be known) was generally accepted by physical organic chemists.

"By 1960, there were indications of trouble for this hypothesis. Many data did not fit either of the two categories, and the associated mechanistic interpretations were clearly wrong in some instances

"My 1961 paper approached the characterization of reactions in a wholly different way, relating reaction rate to the thermodynamic activity of water, and deriving for each reaction a proportionality constant called a  $w$  value The  $w$  values reckoned for 158 sets of data showed 'no particular tendency to group within the two ranges corresponding to the Zucker-Hammett classifications.' I went on to recommend 'that the Zucker-Hammett categories not be used for serious classification of reactions '

"Thus my paper challenged the prevailing paradigm It was not the first to express doubts, but it was the first squarely to recommend abandonment It became controversial, and somecited it to decry it. Gradually the Zucker-Hammett hypothesis faded and was superseded by a group of methods, different but philosophically compatible, for dealing with such kinetic data. The method I advocated in 1961 is not much used today, but several of the successor methods (including one by Olsen and myself<sup>2</sup>) derive from it.

"Kuhn says that almost always the men who introduce a new paradigm have been either very young or very new to the field whose paradigm they change. Such men, being little committed by prior practice to the traditional rules, are particularly likely to see that those rules no longer define a playable game and to conceive another set that can replace them. It so happens that I had taken part in only one investigation of limited scope in that research area before developing the ideas published in the 1961 paper."

#### REFERENCES

1. Kuhn T S. *The structure of scientific revolutions*. University of Chicago Press, 1962.172 pp.
2. Bunnett J F & Olsen F P. Linear free energy relationships concerning reaction rates in moderately concentrated mineral acids. *Can. J. Chem.* **44**:1917-31, 1966.