# Book Review

**The Kinetics of the Oxidation-Reduction Reactions of Uranium, Neptunium, Plutonium, and Americium in Aqueous Solutions.** By T. W. Newton. TID-26506 U.S. Energy Research and Development Administration Critical Review Series, Springfield, Virginia. 132 pp. $5.45.

This is an excellent monograph. The book is a review and, in part, a critique of the reported oxidation-reduction reactions of the lighter actinide ions in aqueous solution. A total of 250 references, some as recent as late 1973 but extending over 30 years, are included.

The work is of interest not only to the specialist but to any chemist curious about the subject. The latter audience is reached by the inclusion of a chapter entitled "Preliminary Considerations," in which a brief but sufficient summary and discussion of the topics particularly useful for the understanding of oxidation-reduction rate data are presented. In addition, the third chapter addresses 12 specific reactions in depth and illustrates how a variety of experimental probes can be used to obtain mechanistic information. The unavoidable ambiguity in deciphering a unique mechanism for a reaction, especially in aqueous solution, is carefully analyzed.

The fourth chapter considers the reactions among the ions of uranium, neptunium, and plutonium. The following brief chapter on the effect of self-irradiation in plutonium solutions serves as a warning that radiolysis effects become progressively important and experimentally troublesome as the activity of the nuclide under study increases. This caution is repeated in the sixth chapter, which deals with the limited number of reactions of americium ions that have been investigated.

The next three chapters deal with ionic strength effects, thermodynamic considerations of the overall reactions and the activation processes, and an excellent analysis of empirical correlations. A large amount of kinetic data is available for the oxidation-reduction reactions of the actinide ions. The author has carefully tested empirical correlations using hydrogen ion dependencies, the various activation parameters, and the entropies of activated complexes. This analysis is both intriguing and rather novel. What emerges is a clear picture of not only the potential but also the limitations of these empirical correlations. They give hope to the individual investigator that his limited contributions may someday provide important pieces in the puzzles of science. At the same time, the necessity for accurate and extensive data to avoid premature and unreliable correlations is amply illustrated.

The final chapter alone is worth the price of the book, at least to the specialist. In this "catalog of reaction rates" are summarized typical experimental conditions, rate data (including the form of the rate expression, values of the rate parameters at a designated temperature, enthalpies of activation if determined, and any catalysis observed), and references for 240 reactions. The tables are organized by either oxidation or reduction of a particular actinide ion, and the other reactants are tabulated within each table alphabetically. Thus, the user can quickly find whether a reaction of interest has been studied, and if so find a synopsis of the results at a glance or locate the original paper if more detailed information is desired. Similar "catalogs" for reactions of, for instance, the *d*-block transition metal ions or oxyanions would be invaluable.

In the Foreword, Major General Ernest Graves points out the basic need for detailed knowledge of the chemical behavior of the heavy elements in nuclear energy activities. Newton also mentions this concern in his Introduction. This is a valid and sobering consideration, particularly in view of the current apparent conflict between energy requirements and the desire for a clean and safe environment. However, the potential value of the monograph extends beyond this rationale for investigating actinide chemistry. This field has been extensively developed, probably in more depth than the chemistry of the transition elements. Unfortunately, this fact is not generally appreciated, and this work may serve to partially correct the situation. There also seems to exist an attitude in many chemists that heavy element chemistry is rather specialized and unique, bearing little relevance to the behavior of the more familiar elements. The results presented and the conclusions drawn in this monograph clearly reaffirm that chemistry is not compartmentalized. Oxidation-reduction reactions of the actinide ions are closely related to reactions of the ions of the lighter elements.

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