

BOOK REVIEWS

Selection of books for review is based on the editor's opinions regarding possible reader interest and on the availability of the book to the editor. Occasional selections may include books on topics somewhat peripheral to the subject matter ordinarily considered acceptable.



The Kinetics of the Oxidation-Reduction Reactions of Uranium, Neptunium, Plutonium, and Americium in Aqueous Solutions

<i>Author</i>	T. W. Newton
<i>Publisher</i>	U.S. Energy Research and Development Administration
<i>Pages</i>	131
<i>Price</i>	\$5.45
<i>Reviewer</i>	Jack L. Ryan

The purpose of this book, as stated by the author, is to provide chemists with a complete survey of the kinetics of oxidation-reduction reactions of uranium, neptunium, plutonium, and americium in aqueous solutions. The author has, in my opinion, accomplished his objective in a thorough, concise, and well-balanced manner. All these elements have either four or five oxidation states that can exist in aqueous solutions. Although some of these oxidation states, such as U(V) and Am(IV), are of relatively low stability in aqueous solution under most conditions, they may be important intermediates in oxidation-reduction reactions. On the other hand, four oxidation states of plutonium can coexist at equilibrium in certain dilute acid solutions. Since the rates of the oxidation-reduction reactions of these elements can vary widely depending on the oxidation states involved and the nature of the oxidizing or reducing agents used, the rates of these reactions can

assume considerable importance in the chemistry of the elements. Information on these rates is of importance in many phases of aqueous chemical processing of actinides, in analysis, in management of actinide containing wastes, and in the behavior of actinides in the environment.

The book does not purport to be a treatise on the general theory of kinetics of oxidation-reduction reactions or on actinide element chemistry, yet presents enough of this general background theory to be very helpful to the reader who is not an expert in the field. This is particularly true with regard to Secs. 2-2 through 2-6, which give a good brief review of oxidation-reduction reaction mechanisms and kinetics. In the brief discussion of use of absorption spectra to follow reactions, including the table of absorptivities, it would have been desirable if the author had noted that the absorptivities usually change with the nature and, except in the case of perchloric acid, the concentration of the acid. The author then proceeds, in Chap. 3, to treat 12 typical reactions in detail as to methods of rate determination, different rate laws, and different ways of interpreting these rate laws. The data for the multitude of other reactions that have been studied to varying degrees are then presented in largely tabular form in Chaps. 8 and 10. This is a very reasonable approach to the presentation of this subject.

Reactions among the actinide ions, including the important disproportionation reactions, are covered separately in Chap. 4. The rates of radiolytic self-reduction of plutonium

ions are discussed in Chap. 5. This is an important aspect of plutonium solution chemistry and becomes even more important for power-reactor-grade plutonium than indicated for the ^{239}Pu data. First-generation power-reactor-grade plutonium will have a specific activity approximately 4 times and the third-generation plutonium approximately 12 times that of ^{239}Pu , and radiolytic reduction will be a much more important factor with this material. In this regard, it would have been desirable for the author to have noted that the data that he cites in Chap. 5 are not for isotopically pure ^{239}Pu . As a result, the G values given may be 10 to 30% high, since at least in most of the work, there does not appear to have been any attempt to correct for isotopic composition.

The reactions of americium ions are logically treated separately in Chap. 6 because of the extensive radiation effects. Useful empirical correlations of the rate data are presented in Chap. 9 to help identify factors that influence the activation parameters.

Overall, the book appears to be very thorough, well organized, and well written. There are very few typing errors. Perhaps a glossary of symbols with reference to the page where they are defined might have been helpful to the occasional user.

The book should prove to be a very valuable reference work. It is appropriate that it appears now at a time when funding for basic actinide chemistry studies has decreased, and that it is written by a man who has been actively involved in the field over the period in which most of the

work has been performed. This publication should be in the libraries of all facilities where basic or applied actinide chemistry is studied or used as well as on the bookshelves of those working in various aspects of the field of actinide solution chemistry. It should also be a useful addition to the libraries of other institutions where the kinetics of oxidation-reduction reactions in solution are studied.

Jack L. Ryan is a research associate in the Chemical Technology Department of the Pacific Northwest Laboratories of Battelle Memorial Institute in Richland, Washington. He has been active in basic and applied actinide chemistry research for 20 years. His chief areas of research have included applied and basic studies of actinide ion exchange and solvent extraction, actinide and lanthanide coordination chemistry, absorption spectroscopy of actinide and lanthanide compounds and complexes, and systematics of actinide and lanthanide oxidation states and oxidation potentials.

Isotope Techniques in Groundwater Hydrology 1974, Volumes I and II
(Proceedings of an International Atomic Energy Agency Symposium)

Publishers Unipub, Inc. (1974)
Price \$24.00 each volume
Pages Vol. I, 504; Vol. II, 499
Reviewer Donald G. Jacobs

The use of isotopes in groundwater hydrology began with the use by Willard Libby of ^{14}C , and later ^3H , for dating. Isotope techniques in groundwater hydrology have become more refined over the past few decades and have been extended to nonradioactive isotopes.

This two-volume book represents the proceedings of the fourth symposium on the subject of isotope hydrology organized by the International Atomic Energy Agency (IAEA) and held in Vienna on March 11-15, 1974, and includes papers devoted to the development and application of isotope techniques. Unlike the pre-

ceding symposia in this series, this symposium and proceedings were limited to groundwater hydrology.

The symposium was attended by 196 participants from 38 countries and 5 international organizations. The proceedings consists of 51 papers presented at the symposium and organized into 7 subject areas. As typical of the proceedings of IAEA meetings, formal discussion of the papers that took place at the meeting is included.

The 27 papers in Vol. I discuss the results of studies in which measured concentrations of environmental isotopes were used in conjunction with classical hydrologic measurements in interpretation of local and regional hydrology. Tritium and ^{14}C are useful in studies of the dynamics of hydrologic systems. Measurements of these radioisotopes provide an estimate of the apparent age of the water and, in conjunction with other hydrologic measurements, can be used to estimate rates of recharge. Further refinement on the rate of recharge and the direction and velocity of flow is possible by considering spatial distribution of concentrations and relating these to the concentration history of recharge waters. Measurement of ^{13}C provides a means for adjustment of ages determined by ^{14}C .

Stable environmental isotopes (^2H and ^{18}O) are useful in determining the origin of recharge waters. The variation of ^{18}O concentration with altitude allows the hydrologist to determine the altitude of the recharge zone. Deuterium and ^{18}O measurements, in conjunction with determination of the age of water in various formations, can be used to infer climatic changes in the region of study.

Measurement of isotopic compositions in geothermal waters is useful in determining the origin and mixing of groundwater sources. Panichi et al. used variations in ^{18}O and ^3H with time in geothermal fields to determine progressive modifications in the field during exploitation. They also suggest that time variations could be useful in checking the effects of reinjection of waste water into the field.

Although the measurement of environmental isotopes provides useful information in groundwater studies, there are some problems in their use and interpretation, and these are

addressed in a number of papers and in the recorded discussions. In fractured formations where rates of movement are fast relative to the rates of mixing, both temporal and spatial variations in concentrations are likely to be greater than in well-mixed systems. Sauzay sampled rainwater falling into and water percolating from lysimeters to establish a relationship between the two. The temporal concentrations in the percolate, as one would anticipate, always show less variation than in the rainwater.

Winograd and Farlekas discuss limitations of assumptions commonly used in interpretation of information on ^{14}C in groundwater systems. They point out that a major source of CO_2 , in addition to that generated in the soil zone, can affect the dissolved carbonate content of water. Also, in thick aquifers, there may be significant variations of water chemistry and isotope chemistry with depth; in studies of such systems, water should be sampled at different depths. They state that regular variations in ^{14}C and $\delta^{13}\text{C}$ down the hydraulic gradient do not guarantee a meaningful interpretation of either absolute or relative groundwater velocities.

Argon-39 techniques are useful for dating water as the $t_{1/2}$ of 269 yr fills the gap between ^3H ($t_{1/2} = 12.3$ yr) and ^{14}C ($t_{1/2} = 5730$ yr). Argon is a noble gas and thus exhibits simple geochemical and hydrologic behavior. Isotopic ratios of $^{234}\text{U}/^{238}\text{U}$, $^{34}\text{S}/^{32}\text{S}$, and $^{15}\text{N}/^{14}\text{N}$ also can be used to provide useful information in hydrologic studies.

Most of the papers deal with studies of particular groundwater systems and are generally of more interest to hydrologists than to the typical member of the American Nuclear Society (ANS). The papers by Isaacson et al. and by Robertson are of interest to ANS members since they represent work undertaken to describe the movement of radionuclides discharged into the ground. Studies at the Hanford reservation indicate that meteoric water does not percolate to the water table, but rather moves downward only a few meters during autumn and winter and is removed by evaporation and evapotranspiration during the summer. There are also several papers devoted to further development and application of mathematical