Chemical Thermodynamics of Neptunium and Plutonium

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Preface

Unlike earlier books in this series, this review describes the selection of chemical thermodynamic data for species of two elements, neptunium and plutonium. Although this came about more by circumstance than design, it has allowed for a more consistent approach to chemical interpretations than might have occurred in two separate treatments. It has also drawn attention to cases where the available data do not show expected parallels, and where further work may be useful to confirm or refute apparent differences in the behaviour of neptunium and plutonium. This volume has taken more than ten years to compile. The combined neptunium and plutonium groups, selected by Anthony Muller, the originator of the TDB project, first met at Saclay, France in April 1988. Subsequent meetings were held at Pinawa, Canada in September 1990, at Saclay in February 1992, and at Issy-les- Moulineaux, France in March 1994 and December 1997. Smaller working sub-groups met in Chicago (1994 and 1996) and Issy-les-Moulineaux (1995 and 1996). The logistics and financing of the TDB project has meant the NEA itself has had difficulties in editorial preparation of more than one volume at a time, and the current volume has passed through the hands of four successive TDB co-ordinators, Hans Wanner (who later joined the neptunium/plutonium TDB team as a reviewer), Ignasi Puigdomenech, Amaia Sandino and Erik Östhols. The latter two have done the bulk of the work in combining the reviewers' drafts and seeing the book through to its final form. Several of the reviewers worked on other elements for the TDB; this overlap delayed work on neptunium and plutonium, but has enhanced the consistency of the TDB as a whole. Despite the extended time-frame, most of the original participants in the project have persisted through to its completion - perhaps an indication of the importance the authors have attached to the review. During the time the work was being done, a large number of excellent, relevant studies have been reported in the literature, many based in the world-wide efforts directed toward management of nuclear fuel waste. These papers have helped strengthen, but have to some extent delayed this publication. Any chemical thermodynamic database does no more than represent a survey of what is known at a particular time. The time required to carefully compile and consider data dictates that any database is at least slightly "out-of-date" by the time it appears in print. The current review is no exception. Although an arbitrary "cut-off" date of mid-1996 was set for papers used in this review, a few later papers have been included. The large number of co-authors has resulted in less consistency in style and depth of discussion than in some previous volumes. We hope readers do not find this unduly distracting. Although almost all of the authors contributed text and comments to many of the chapters, primary responsibility for the different chapters was divided as follows. William Ullman and Jim Sullivan prepared the sections on sulphato complexes and on plutonium carbonates, Hans Wanner the sections on aqueous halide and thiocyanate complexes, Kastriot Spahiu the sections on nitrato and phosphato complexes, Pierre Vitorge the extensive section on neptunium carbonates (he also extensively rei viewed several of the other sections), Heino Nitsche the initial drafts of the aqua-ion sections, and Paul Potter the sections

on nitrides. Malcolm Rand prepared the sections on carbides and, with Jean Fuger, the sections on solid and gas phase halides. He and the chairman drafted the sections on oxides, and the chairman prepared the sections on hydrolysis with help from Jan Rydberg (who also provided his expertise in extraction techniques to the other reviewers as required). Experimental chemical thermodynamics is not a particularly popular topic in modern scientific circles. Because of safety and regulatory constraints, work on the chemistry of transuranium elements is particularly slow, and therefore costly. Fewer and fewer laboratories are capable of carrying out such measurements, and of having the luxury of time to check and recheck their values. It was therefore distressing to find that much of the work that has been done was incompletely documented. Often the reviewers have had to pass over what were probably good studies because interpretations had been used that are now known to be incorrect, and the raw data were unavailable for reinterpretation (sadly, this was the case even for several studies done in the late 1980s). As is the case for databases for many other elements, “key” values often are based on a single experiment or even more tenuously on a chain of uncorroborated experimental values. Some of the values for the plutonium aqua ions are particularly glaring examples. Although we have assigned uncertainties, there is no satisfactory way of dealing quantitatively with this problem.

Chalk River, Canada, November 2000 Robert Lemire, Chairman

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Also at the NEA, Stina Lundberg has diligently shepherded the draft into its final form over the last year of the project, and Cecile Lotteau deserves credit for much of the layout work for the volume done between 1995 and 1997. Claes Nordborg has helped maintain support for the project through many personnel changes at the NEA. Pierre Vitorge wishes to express his appreciation to Helena Capdevila of the CEA for many helpful discussions. Robert Lemire thanks the library staff at both Chalk River iii iv ACKNOWLEDGEMENTS and Whiteshell Laboratories of AECL for their literature searches and assistance in obtaining copies of many references.

The entire manuscript of this book has undergone a peer review by an independent international group of reviewers, according to the procedures in the TDB-6 guidelines, available from the NEA. The peer reviewers have viewed and approved the modifications made by the authors in response to their comments. The peer review comment records may be obtained on request from the OECD Nuclear Energy Agency. The peer reviewers are:

Dr. Jacques Bourges	Verrières-le-Buisson, France
Dr. Trygve Eriksen	Department of Chemistry, Nuclear Chemistry,Royal Institute of Technology, Stockholm, Sweden
Dr. Rudy J. M. Konings	European Commission, Joint Research Centre, Institute for Transuranium Elements, Karlsruhe, Germany
Dr. Kenneth K. Nash	Chemistry Division, Argonne National Laboratory, Argonne, Illinois, U.S.A.
Dr. Dean E. Peterson	Los Alamos National Laboratory, MST Superconductivity Technology Center, Los Alamos, New Mexico, U.S.A.
Dr. Dhanpat Rai	Battelle, Pacific Northwest National Laboratory, Richland, Washington, U.S.A.

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