

# *The Chemical Thermodynamics of Actinide Elements and Compounds*

## *PART 2* *The Actinide Aqueous Ions*

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J. FUGER  
F.L. OETTING



INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1976

# THE CHEMICAL THERMODYNAMICS OF ACTINIDE ELEMENTS AND COMPOUNDS

## Part 2 The Actinide Aqueous Ions

by

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OF ACTINIDE ELEMENTS AND COMPOUNDS**

**Part 2  
The Actinide Aqueous Ions**

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## FOREWORD

The production of nuclear energy involves many essentially chemical problems the solution of which may well depend upon the thermodynamic analysis of the chemical interaction. The fuel/fission-product/cladding interface is a typical example of a site where factors governing the lifetime and/or the safety of reactor operations are involved. To prevent cladding failure the potential chemical interactions between fuel, fission products and cladding must be predicted. Moreover, both the evaluation of the transport properties of nuclear fuels under steep temperature gradients and the prediction of the conditions obtained in a hypothetical sub-critical excursion require a detailed knowledge of the thermodynamic properties of the nuclear fuels. These are only a few of the many examples that could be found of the application of chemical thermodynamic data to the nuclear industry.

To assist reactor engineers and physical scientists, critically evaluated compilations of thermodynamic data have been assembled from time to time by thermodynamic experts. In the late 1940s, L. Brewer and colleagues produced a pioneering series of papers dealing with the thermodynamic properties of nuclear materials. They were published in 1949 by McGraw-Hill, New York, in Volume 14B of the United States Atomic Energy Commission's National Nuclear Energy Series. This was followed more than ten years later, in 1963, by "The Uranium-Carbon and Plutonium-Carbon Systems: a Thermochemical Assessment", published by the International Atomic Energy Agency as Technical Reports Series No.14, a report from a panel convened by the Agency in 1962. The Agency's decision to publish compilations of physico-chemical data of substances important to reactor technology resulted in a series of monographs edited by O. Kubaschewski. These have appeared as Special Issues of the Agency's Atomic Energy Review, giving the physico-chemical properties of each element's compounds and alloys. So far the following have been published: Special Issue No.1, on plutonium, 1966; No.2, on niobium, 1968; No.3, on tantalum, 1972; No.4, on beryllium, 1973; No.5, on thorium, 1975. Four more monographs in this series are planned: on molybdenum, zirconium, hafnium and titanium.

For the actinide series of elements themselves (thorium, protactinium, uranium, neptunium, plutonium, americium, etc.), critical assessments include, in addition to the work published by Brewer and the Atomic Energy Review Special Issues, the following two publications: "The Thermodynamic Properties of Uranium Compounds", by M.H. Rand and O. Kubaschewski, published by Oliver and Boyd, London, in 1963, and "The Chemical Thermodynamic Properties of Plutonium Compounds", a paper by F.L. Oetting in Chemical Reviews, Vol.67 (1967), pp.261-297.

Other surveys of the thermodynamic properties of certain actinide materials have indeed appeared since 1967, but they are either of limited breadth, or have not been critically evaluated, and even taken as a whole, these data are not in a format ideally suited for either science or technology. Moreover, considerable experimental thermodynamic data on the actinide elements and their compounds have been reported in the last 7-8 years. Hence, nuclear engineers and/or physical scientists concerned with the problems in nuclear systems urgently need a reliable, self-consistent, up-to-date set of thermodynamic data.

To respond to this need, the International Atomic Energy Agency has initiated a programme of compilation on an international basis. To co-ordinate the effort, the Agency has established an Advisory Board consisting of F.L. Oetting (Division of Research and Laboratories, IAEA, Vienna), V. Medvedev (Institute for High Temperatures, Moscow, USSR), M.H. Rand (Atomic Energy Research Establishment, Harwell, UK) and E.F. Westrum, Jr. (University of Michigan, Ann Arbor, Michigan, USA), to provide editorial direction and review for the overall project and ensure compatibility with extant major thermodynamic compilations, standards, reference states, etc.

Eleven groups of authors, from widely separated institutions and laboratories — but with a common aim and high qualifications for the task — are engaged in the preparation of critical analyses of available thermodynamic experimental data and in the extension and estimation of thermodynamic data where experimental values are not available. The material will be published in eleven parts, and as far as possible each part will contain tables of thermodynamic functions pertaining to the crystal, liquid and gas phase of each compound relevant to that part. An extended temperature range will be covered so that the work will be of maximum benefit to the nuclear engineer and/or nuclear scientist.

To encourage the use and understanding of SI units, the data of the thermochemical tables, printed at the end of each part, appear on the left-hand page in conventional units and on the right-hand page in SI units.

The following list gives the title of each part and the names of the compilers:

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## GENERAL INFORMATION

This series is divided into eleven Parts, each Part consisting of the main text and an Appendix. The text gives a critical evaluation of published data found in the literature up to early 1976.

The Appendix of each Part contains the thermodynamic tables for the actinide materials pertaining to that Part. These tables, using the fundamental thermodynamic equations, provide consistent values for the standard heat capacity ( $C_p^\circ$ ), standard entropy ( $S^\circ$ ), standard 'tempered' Gibbs energy ( $[G^\circ(T) - H^\circ(298)]/T$ ), standard enthalpy increment ( $H^\circ(T) - H^\circ(298)$ ), standard enthalpy of formation ( $\Delta H_f^\circ$ ) and standard Gibbs energy of formation ( $\Delta G_f^\circ$ ) at 100-degree intervals from 300 K to the highest temperature where reliable thermodynamic information is believed to exist. The three decimal places provided may not be justified from the standpoint of absolute accuracy; however, these numbers are retained for internal consistency and to permit interpolation.

### A. FUNDAMENTAL CONSTANTS

The set of values for the fundamental constants recommended by the Committee on Data for Science and Technology (CODATA), International Council of Scientific Unions, Task Group on Fundamental Constants (CODATA Bulletin No.11, December 1973) are used. The more commonly used quantities are listed below.

<u>Quantity</u>	<u>Symbol</u>	<u>Value</u>	<u>Unit</u>
Speed of light in vacuum	c	$2.99792458 \times 10^8$	$\text{m} \cdot \text{s}^{-1}$
Boltzmann constant	k	$1.380662 \times 10^{-23}$	$\text{J} \cdot \text{K}^{-1}$
Planck constant	h	$6.626176 \times 10^{-34}$	$\text{J} \cdot \text{s}$
Avogadro constant	N	$6.022045 \times 10^{23}$	$\text{mol}^{-1}$
Faraday constant	F	$9.648456 \times 10^4$	$\text{C} \cdot \text{mol}^{-1}$
Absolute temperature of 0°C	T (0°C)	273.15	K
Molar gas constant	R	8.31441 1.98719 82.0569	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ $\text{cm}^3 \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
Molar volume, ideal gas at 273.15 K, 1 atm	$V_m$	0.02241383	$\text{m}^3 \cdot \text{mol}^{-1}$
Second radiation constant	$c_2 = hc/k$	0.01438786	$\text{m} \cdot \text{K}$

## B. SYMBOLS

am	Amorphous
$C_p$	Molar heat capacity at constant pressure
c	Crystalline state
D	Dissociation energy
E	Internal or intrinsic energy
$\epsilon$	Electromotive force
$G = H - TS$	Gibbs energy
g	Gaseous state
$H = E + PV$	Enthalpy
K	Equilibrium constant
liq	Liquid state
ln	Napierian logarithm to the base e
log	Decadic logarithm to the base 10
M	Molecular weight
P	Pressure
R	Ideal gas constant
S	Entropy
T	Temperature
Vol	Volume

### *Subscripts*

b	Boiling point at 1 atm pressure
eq	Equilibrium position
f	Formation from elements
m	Melting
oxid	Oxidation
p	Constant pressure
r	Reaction
s	Sublimation
soln	Solution (Dissolution)
tran	Transition
v	Vaporization

## C. NOMENCLATURE AND CONVENTIONS

Superscript zeros (<sup>0</sup>) indicate the thermodynamic standard state, defined as the stable state at 1 atm pressure and the temperature under consideration.

Throughout the text and tables, the temperature 298 K refers to 298.15 K. Numerals in brackets or T in brackets denote the temperature.

$[G^0(T) - H^0(298)]/T$  is called the 'tempered Gibbs energy' (base 298 K).

The symbol  $\Delta$  indicates the increment in a given property for a given reaction or process, taken as the value for the final state (or the sum of the products) less that for the initial state (or the sum of the reactants).

All relative atomic masses for the elements are taken from 1971 IUPAC chemical scales based on carbon-12. When the element is not naturally occurring and isotopic data are available, the Atomic Mass Tables of A.H. Wapstra and N.B. Gove, Nuclear Data Tables 9 4-5 (July 1971), are used.

Estimated quantities are denoted by enclosing them in tildes, e.g.  $\sim (145 \pm 10) \sim$ .

The uncertainties in the thermodynamic values given in the text and the thermodynamic functions listed in the tables represent the best estimates of the overall uncertainties in the values at the 95% confidence level.

## D. UNITS

In the text, the thermochemical calorie,

$$1 \text{ cal} = 4.184 \text{ J}$$

is used as the unit of energy, but in the Appendix of each Part the thermochemical tables are provided with both calorie and joule as the energy unit, the latter values being differentiated by coloured print.

The standard atmosphere

$$1 \text{ atm} = 101\,325 \text{ Pa}$$

is used as the pressure unit.

Lattice parameters are reported in ångströms, defined as

$$1 \text{ Å} = 10^{-10} \text{ m}$$



## PART 2

### THE ACTINIDE AQUEOUS IONS

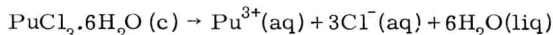
#### 2.1. INTRODUCTION

This Part is concerned with the thermochemistry of actinide ions in solution. We have confined our comments to the thermal behaviour in acid media only, declining for the most part to comment on the thermal phenomena in basic solution because, as a rule, the specific reactions are not clearly defined in such media, resulting in various stages of complexation which in turn leads to a complicated chemical system. Although such behaviour of ions in various media is interesting to an inorganic chemist, it is usually avoided by a competent calorimetrist because one of the essential requirements of precise calorimetry is accurate definition of the reaction. However, we have made an exception in discussing briefly the thermodynamic behaviour of the heptavalent species of neptunium and plutonium which can be stabilized only in basic media.

Calorimetric measurements of actinide metal dissolution in acid media, which for the most part is a well-defined reaction resulting in the formation of a single actinide ion, constitute the basis for this Part as well as for other Parts in this series because the recommended enthalpies of formation of some of these ions are essential in the determination of the enthalpies of formation of the actinide halides and of some other compounds. In a number of instances we have at our disposal direct calorimetric measurements of the enthalpic effect upon oxidation or reduction of ions from one valency state to another, but in many cases electromotive force measurements are the bridge between the thermodynamic properties of the various valency states.

Thermodynamic quantities derived from electromotive force measurements may be less reliable than calorimetric values because the majority of emf measurements are reported as the formal potentials as opposed to the standard potentials which are the desired quantities for the thermodynamic interrelationships for the aqueous ions. In a number of instances, however, corrections to unit activity coefficients have been made and therefore fairly accurate values of the standard potentials are available.

Few direct determinations of the entropies of the actinide ions exist and, up to 1970, the only entropy value experimentally available was that of  $\text{UO}_2^{2+}(\text{aq})$  (Coulter et al., 1940). However, in 1970, Hinchey and Cobble (1970a) determined the enthalpy and Gibbs energy of solution of  $\text{PuCl}_3 \cdot 6\text{H}_2\text{O}(\text{c})$  according to the following reaction:



and obtained the entropy of  $\text{Pu}^{3+}(\text{aq})$  by using the entropy of  $\text{PuCl}_3 \cdot 6\text{H}_2\text{O}(\text{c})$ . The entropy of this salt was estimated from that of the isostructural salt,  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}(\text{c})$ , whose entropy was in turn estimated from low-temperature heat capacity measurements on other lanthanide trichloride hydrates (Hellwege et al., 1959; Pfeffer, 1961a, b; Hellwege et al., 1961; Pfeffer, 1962).



Hinchey and Cobble (1970a) estimated the entropies of the other trivalent actinide ions by assuming that the variation of the entropies with the ionic radii was similar to that observed by them for the trivalent lanthanide ions (1970b). In this estimation, the entropy of each ion was taken as the sum of an electronic term due to the degeneracy of the ground-state, eventually increased by the contribution of thermally populated higher electronic states, and a term depending particularly on the radius of the ion. The latter term was found to be a linear function of the reciprocal of the square of the ionic radii.

We have followed the same procedure in our estimation of the trivalent actinide ions using the most recent data (National Bureau of Standards, Technical Note 270-7, April 1973) for the entropies of the lanthanide ions, which take into account recent findings of magnetic ordering (Wielinga et al., 1967; Lagendijk and Huiskamp, 1973) of the trichloride hydrates below 1 K, and recent data on the ionic radii of the lanthanide and actinide trivalent ions (Peterson and Cunningham, 1967; Morss, 1969; Shannon and Prewitt, 1969; Jones and Choppin, 1969). However, as the derived entropy values of the actinide  $M^{3+}(\text{aq})$  ions other than  $\text{Pu}^{3+}(\text{aq})$  are rather dependent on the set of ionic radii used, we have suitably increased their uncertainty limits.

The entropies of the actinyl ions rest on experimental data on  $\text{UO}_2^{2+}(\text{aq})$  and  $\text{NpO}_2^{2+}(\text{aq})$ . We have considered all the available information on the enthalpy of solution of uranyl nitrate hexahydrate in water and acidic media (see Section 2.5) and have corrected these data for hydrolysis of the uranyl ion in extrapolating to standard conditions. Combining this value with the Gibbs energy of solution and entropy of this salt yielded the accepted value for the entropy of  $\text{UO}_2^{2+}(\text{aq})$ . A new value for the entropy of  $\text{NpO}_2^{2+}(\text{aq})$  has been obtained from solubility data on neptunyl nitrate hexahydrate, the entropy of this salt and the enthalpy of solution in water of neptunyl nitrate hexahydrate (Brand and Cobble, 1970) which we corrected for hydrolysis in the same manner as in the case of the corresponding uranyl salt. The entropy of  $\text{NpO}_2^{2+}(\text{aq})$  has been obtained from that of  $\text{NpO}_2^{2+}(\text{aq})$  with the knowledge of the thermodynamic parameters associated with the reduction of  $\text{NpO}_2^{2+}(\text{aq})$  to  $\text{NpO}_2^+(\text{aq})$  (Brand and Cobble, 1970). The entropies of the other actinyl ions have been estimated, taking into account the magnetic contribution assuming spin-only effect or spin-orbit coupling as done by Brand and Cobble (1970). In the present assessment, these estimated values have only been accepted after verifying that they fit reasonably well with the entropy data which can be derived from a combination of the enthalpies of formation with the existing potential data.

As far as the entropies of the tetravalent ions are concerned, the only experimental value available is that of  $\text{Th}^{4+}(\text{aq})$  which has been obtained very recently (Morss and McCue, 1975). Therefore, the entropies adopted for all the tetravalent ions except  $\text{Th}^{4+}(\text{aq})$  result from combining existing enthalpies of formation with potential data and with the accepted entropies for the other ions. The difficulty of extrapolating to standard conditions and of completely understanding the chemical properties of these highly charged species explains the higher uncertainties for the entropy values of the tetravalent ions.

Nugent and co-workers have established a number of relationships linking the thermodynamic properties of the lanthanide and actinide ions with the electron transfer absorption band energies of their chloro-complexes (Nugent et al., 1969, 1971, 1973b), with the thermodynamic and spectroscopic properties of the metals (Nugent et al., 1973a) and with the amalgamation