

# Experimental thermochemistry of neptunium oxides: $\text{Np}_2\text{O}_5$ and $\text{NpO}_2$

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## HIGHLIGHTS

- We synthesize and characterize  $\text{Np}_2\text{O}_5$  and  $\text{NpO}_2$ .
- Enthalpy of decomposition of  $\text{Np}_2\text{O}_5$  to  $\text{NpO}_2$  agrees with existing thermodynamic data.
- The calorimetric methodology is straightforward and reliable.

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## ABSTRACT

Neptunium (Np) compounds are important in the nuclear fuel cycle because of the buildup and long half-life (2.14 Ma) of Np-237 in nuclear waste, especially during long-term disposal in a geological repository. Neptunium in environmental conditions exists mainly in two oxidation states (+5 and +4) and can substitute for uranium and/or rare earths in solid phases. Yet thermochemical data for solid neptunium compounds are scarce, despite being critical for evaluating the environmental transport of this radioactive and toxic element. Although high temperature oxide melt solution calorimetry has proven very useful in obtaining thermodynamic data for the formation of uranium and thorium oxide materials, it has not yet been applied to transuranium compounds. Continuing a program at Notre Dame to study the thermodynamics of transuranium compounds, we report the first determination of the enthalpies of drop solution of well-characterized neptunium oxides ( $\text{Np}_2\text{O}_5$  and  $\text{NpO}_2$ ) using oxide melt solution calorimetry in molten sodium molybdate solvent at 973 K. The enthalpy of the decomposition reaction,  $\text{Np}_2\text{O}_{5(\text{cr})} = 2\text{NpO}_{2(\text{cr})} + 1/2\text{O}_{2(\text{g})}$  at 298 K, is determined to be  $7.70 \pm 5.86$  kJ/mol, and this direct measurement is consistent with existing thermodynamic data. The calorimetric methodology is straightforward and produces reliable data using milligram quantities of radioactive materials, and can be applied to many other transuranium compounds.

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## 1. Introduction

Neptunium-237 is of concern for the long-term geological disposal of spent nuclear fuel because of its long half-life (2.14 Ma) and potential mobility, especially under oxidizing conditions because the neptunyl ( $\text{NpO}_2^+$ ) ion is soluble in water. Neptunium forms various compounds with peroxide [1], sulfate [2,3], phosphate [4–6], arsenate [4], and other oxyanions, as well as simple

oxides. Studies have shown that neptunium oxides can precipitate from neptunyl solutions under mildly oxidizing conditions [7,8]. Neptunium may also partition into uranyl phases, such as studtite or metastudtite (alteration phases of  $\text{UO}_2$  fuel), by substitution for U(VI) with appropriate charge balance mechanisms [9–13]. Therefore it is crucial to understand the geochemical stability of Np-containing solid materials as well as species in aqueous solution. However, there are very limited reported thermodynamic data for solid neptunium compounds, owing to the scarcity of facilities and techniques that are equipped for handling this radionuclide.

Neptunium exists in environmental conditions primarily in two

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oxidation states (+5 and +4) and has two stable oxides,  $\text{Np}_2\text{O}_5$  and  $\text{NpO}_2$ .  $\text{Np}_2\text{O}_5$  has a monoclinic structure (space group  $P2_1/c$ ) [14] and is stable at low temperature (it decomposes to  $\text{NpO}_2$  and  $\text{O}_2$  between 700 and 973 K [15]), whereas  $\text{NpO}_2$  in the cubic fluorite structure (space group  $Fm\bar{3}m$ ) is stable to its melting point of  $3070 \pm 62$  K [16]. The enthalpy of formation of  $\text{Np}_2\text{O}_5$  has been measured by acid solution calorimetry by Belyaev et al. ( $\Delta_f H^\circ_{298}(\text{Np}_2\text{O}_5) = -2148 \pm 12$  kJ/mol) [17] and by Merli and Fuger ( $\Delta_f H^\circ_{298}(\text{Np}_2\text{O}_5) = -2162.7 \pm 9.3$  kJ/mol) [18]. However, these reported values are in poor agreement. The only reported enthalpy of formation of  $\text{NpO}_2$  was measured by oxygen bomb calorimetry by Huber and Holley ( $\Delta_f H^\circ_{298}(\text{NpO}_2) = -1074.2 \pm 2.5$  kJ/mol) [19], using 2 g of material. The heat capacities of  $\text{Np}_2\text{O}_5$  (from 350 to 750 K) [20] and  $\text{NpO}_2$  (from 5 to 1770 K) [21–24] have also been measured. However, the low temperature (0–298 K) heat capacities of  $\text{Np}_2\text{O}_5$ , needed to obtain standard entropies, have not been reported. A recent study suggests the existence of  $\text{Np}_4\text{O}_9$  with O clustering to fill gaps between fluorite-structured  $\text{NpO}_2$  and layer-structured  $\text{Np}_2\text{O}_5$  [25]. This phase is difficult to synthesize as pure material and has not been fully characterized, so it is not included in the present study.

High temperature oxide melt solution calorimetry has been successfully utilized to study the thermochemistry of actinide oxides containing thorium and uranium [26–29]. Here, we describe the further development of this technique at the University of Notre Dame to study the formation enthalpies of neptunium compounds. Neptunium oxides ( $\text{Np}_2\text{O}_5$  and  $\text{NpO}_2$ ) have been synthesized and characterized for calorimetric study. Their drop solution enthalpies (enthalpy of reaction in which a solid oxide pellet is dropped from room temperature into a molten oxide solvent at calorimeter temperature and dissolved) into molten sodium molybdate solvent at 973 K have been measured. The decomposition enthalpy of  $\text{Np}_2\text{O}_5(\text{cr}) = 2\text{NpO}_2(\text{cr}) + 1/2\text{O}_2(\text{g})$  at 298 K is determined to be  $7.70 \pm 5.86$  kJ/mol. This value agrees well with those calculated using previously reported formation enthalpies of the two neptunium oxides. These experiments are a first step in the calorimetric study of heats of formation of more complex neptunium materials.

## 2. Materials and methods

### 2.1. Material preparation

**Caution:** Neptunium-237 is radioactive and it decays by emission of alpha radiation. Its decay product is protactinium-233, which emits a strong gamma that is dramatically more penetrating than alpha. Therefore all experiments were done in purpose-designed laboratories at the University of Notre Dame with proper equipment. Conduction of experiments of this sort requires monitoring of the area and personnel, and a comprehensive program of radiation worker training and institutional oversight.

$\text{Np}_2\text{O}_5$  was prepared by hydrothermal reaction of  $\text{NpO}_2^+$  solutions with natural calcite crystals, as previously reported by our group for samples used for single-crystal structure determination of this compound [14]. The reactants were placed in Teflon cups with screw-top lids that were then placed inside Teflon-lined 125 mL stainless steel Parr reaction vessels, together with water to provide counter pressure in the outer vessel. The vessels were heated at 473 K for 7 days. Monitoring for unintended release of radionuclides is essential during disassembly of this apparatus, which should be conducted in a fume hood under negative pressure relative to the laboratory ambient. Dark brown  $\text{Np}_2\text{O}_5$  crystals were recovered, and washed using 1N HCl to remove any remaining calcite, followed by washing with ultrapure  $\text{H}_2\text{O}$ . The crystals were

dried inside a glove box.  $\text{NpO}_2$  was prepared by the decomposition of  $\text{Np}_2\text{O}_5$  during heating to 1173 K in  $\text{N}_2$ .

### 2.2. Thermogravimetric analysis

Thermogravimetric analyses were performed using about 10 mg of dried  $\text{Np}_2\text{O}_5$  crystals in a TA Instruments Q50 located in a radiological hood from 303 K to 1173 K at a heating rate of 5 K/min under  $\text{N}_2$ . The sample was held at 423 K for 30 min to eliminate surface water on the  $\text{Np}_2\text{O}_5$  crystals. The mass loss was in agreement with the end product being  $\text{NpO}_2$  (Fig. S1).

### 2.3. Powder X-ray diffraction (PXRD)

$\text{Np}_2\text{O}_5$  and  $\text{NpO}_2$  (remaining powder from TGA of  $\text{Np}_2\text{O}_5$  crystals) products were ground using an agate mortar and pestle inside a glove box under negative pressure with respect to ambient and were deposited onto an airtight sample holder that provides containment of the material. PXRD patterns were collected from 5 to 90° (2 theta) with  $\text{CuK}\alpha$  radiation using a Bruker D8 Advance diffractometer with a step width of 0.02° and 1 s counting per step (Fig. S2 and S3), and repeated three times to increase the peak to background ratio. The patterns were processed using PDF-4+ to confirm the identities of both neptunium oxides and the absence of secondary phases.

### 2.4. Calorimetry

Enthalpies of drop solution of the neptunium oxides into molten sodium molybdate ( $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ ) at 973 K were measured using a Setaram AlexSYS 1000 high temperature Tian-Calvet calorimeter. The calorimeter was calibrated using the heat content of 5 mg  $\alpha$ - $\text{Al}_2\text{O}_3$  pellets [30–32]. In order to minimize the risk of neptunium dispersal, silica glass crucibles were used as the molten solvent container (rather than platinum), so that the solidified sodium molybdate solvent and the crucibles are suitable for disposal or neptunium recovery as a single unit after the experiment. The sodium molybdate melt is not corrosive to the silica crucibles. Operating procedures for calorimetric experiments using neptunium materials were first developed for non-radioactive samples, and personnel completed multiple non-radioactive experiments of this sort before transitioning to hot work. The neptunium oxide sample pellets were prepared in a designated negative pressure glove box and were transported to the nearby calorimetry lab in triple containment. For each experiment, about 5 mg of neptunium oxides were pressed into a 1.5 mm diameter pellet, weighed accurately on a Mettler-Toledo XSE105 microbalance ( $\pm 0.01$  mg), and dropped into 10 g of molten sodium molybdate solvent contained in silica glass crucibles in the calorimeter. The calorimetric assembly was flushed continuously with oxygen at 43 mL/min and oxygen was bubbled in the molten solvent at 5 mL/min through silica glass tubes to facilitate dissolution of neptunium oxides and provide an oxidizing atmosphere.

### 2.5. UV–Vis spectroscopy

Sodium molybdate solvent containing dissolved neptunium oxide was dissolved in ultrapure  $\text{H}_2\text{O}$  in air, with dissolution complete in a few minutes. UV–vis spectra were collected immediately after dissolution from 400 to 1300 nm at room temperature using a Jasco V-670 spectrophotometer (Fig. S4).

## 3. Results

Initially,  $\text{Np}_2\text{O}_5$  was prepared for study, and  $\text{NpO}_2$  was

subsequently produced by heating  $\text{Np}_2\text{O}_5$ . PXRD confirmed that the starting material was  $\text{Np}_2\text{O}_5$ , with the pattern agreeing with that calculated using the previously reported single crystal X-ray structure [14]. Thermogravimetric analysis (TGA) of  $\text{Np}_2\text{O}_5$  crystals (during which the sample was held at 423 K for 30 min) indicated incorporation of a small amount of water in the oxide, corresponding to composition  $\text{Np}_2\text{O}_5 \cdot 0.077\text{H}_2\text{O}$ . Decomposition of  $\text{Np}_2\text{O}_5$  initiates at about 573 K and is complete above 973 K under  $\text{N}_2$ , with a heating rate of 5 K/min, consistent with previous reports [15]. Bagnall and Laidler reported that  $\text{Np}_2\text{O}_5$  persists to 693 K under vacuum [33]. Decomposition of  $\text{Np}_2\text{O}_5$  to  $\text{NpO}_2$  is reported to occur between 703 and 973 K, depending on  $\text{O}_2$  pressure [34]. Richter and Sari showed that the conversion is irreversible (consistent with thermodynamic data, see discussions below) and that  $\text{NpO}_2$  remains stoichiometric to 1743 K [15]. TGA revealed that the weight loss through heating to 1073 K was 4.0%, indicating that the remaining material was  $\text{NpO}_2$  (calculated weight loss for  $\text{Np}_2\text{O}_{5(\text{cr})} = 2\text{NpO}_{2(\text{cr})} + 1/2\text{O}_{2(\text{g})}$  is 2.9%). PXRD confirmed the heated powder to be  $\text{NpO}_2$ .

The calorimetric data for each drop of  $\text{Np}_2\text{O}_5 \cdot 0.077\text{H}_2\text{O}$  and  $\text{NpO}_2$  samples are listed in Table 1. Both neptunium oxides dissolved quickly in the sodium molybdate solvent at 973 K, and the calorimetric baseline returned to the starting position within 20 min.  $\text{Np}_2\text{O}_5 \cdot 0.077\text{H}_2\text{O}$  gave a small heat effect of less than 0.5 J per experiment, while  $\text{NpO}_2$  gave an even smaller heat effect of less than 0.05 J per experiment. The intrinsically small drop solution enthalpies of both neptunium oxides require a highly stable baseline during the experiments. As a result, only four of eight experiments for  $\text{Np}_2\text{O}_5 \cdot 0.077\text{H}_2\text{O}$  and four of five for  $\text{NpO}_2$  were appropriate for further calculations. The four drops of each sample gave  $\Delta H_{\text{DS}}(\text{Np}_2\text{O}_5 \cdot 0.077\text{H}_2\text{O}) = 39.63 \pm 5.34$  kJ/mol, and  $\Delta H_{\text{DS}}(\text{NpO}_2) = 7.81 \pm 1.22$  kJ/mol. The calorimetric method proved to be straightforward and can be applied to other neptunium compounds.

The oxidation states of neptunium in the molten sodium molybdate solvent after each experiment are crucial for the interpretation of the calorimetric data. Hence, the solvent with dissolved neptunium oxides after being cooled to room temperature was dissolved in water and its UV–Vis spectrum was collected immediately. The final oxidation states of both neptunium oxides in the sodium molybdate solvent were determined to be pentavalent (Fig. S4). Therefore it is possible to use the thermochemical cycles listed in Tables S1 and S2 to calculate the enthalpies of reactions involving both neptunium oxides. We note that, since enthalpy is a state function, as long as the final state of neptunium is well defined as pentavalent, it is irrelevant, from the thermodynamic point of view, whether  $\text{Np}_2\text{O}_5$  initially begins to decompose to  $\text{NpO}_2$  on being dropped into the melt before dissolving, with re-oxidation upon dissolution at 973 K, or whether it dissolves directly.

**Table 1**  
Drop solution enthalpies of  $\text{Np}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  and  $\text{NpO}_2$  into molten sodium molybdate ( $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ ) solvent at 973 K.

$\text{Np}_2\text{O}_5 \cdot n\text{H}_2\text{O}$		$\text{NpO}_2$	
Mass (mg)	$\Delta H_{\text{DS}}$ (kJ/mol)	Mass (mg)	$\Delta H_{\text{DS}}$ (kJ/mol)
5.41	33.91	5.09	6.29
5.54	46.40	6.19	9.01
6.47	37.32	5.57	8.55
5.96	40.90	6.17	7.38
Average <sup>a</sup>	39.63		7.81
Error <sup>b</sup>	5.34		1.22
Error (%) <sup>c</sup>	13.48		15.68

<sup>a</sup> Mean of the experiments listed.

<sup>b</sup> Two standard deviations of the mean.

<sup>c</sup> The uncertainty at a 95% level of confidence.

**Table 2**

Comparison of the drop solution enthalpy, and heat of solution among actinide oxides into molten sodium molybdate ( $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ ) solvent at 973 K.

Phase	$\Delta H_{\text{DS}}$	$\Delta H_{\text{HC}}^a$	$\Delta H_{\text{S}}$
$\text{NpO}_{2.5}$	$17.11 \pm 2.67^{b,c}$	54.63	$-37.52 \pm 2.67$
$\text{NpO}_2$	$7.81 \pm 1.22^c$	53.04	$-45.23 \pm 1.22$
$\gamma\text{-UO}_3$	$9.49 \pm 1.53$ [43]	64.22	$-54.73 \pm 1.53$
$\text{UO}_2$	$-136.4 \pm 2.3$ [43]	52.80	$-189.2 \pm 2.3$
$\text{ThO}_2$	$0.89 \pm 0.48$ [43]	49.50	$-48.61 \pm 0.48$

<sup>a</sup> Heat content of oxides from 298 K to 973 K calculated using  $C_p$  data from Konings [35].

<sup>b</sup> Values for  $\text{NpO}_{2.5}$  are half those for  $\text{Np}_2\text{O}_5$ . All data are in kJ/mol.

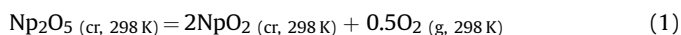
<sup>c</sup> This work.

## 4. Discussion

To obtain  $\Delta H_{\text{DS}}$  of anhydrous  $\text{Np}_2\text{O}_5$ , the effect of the small amount of water, which is presumably on the surface of the crystals, must be taken into account. Assuming physical adsorption, the water adsorption enthalpy is  $-44.0$  kJ/mol, which is the heat of water vapor condensation at 298 K. Thus,  $\Delta H_{\text{DS}}(\text{Np}_2\text{O}_5)$  is calculated to be  $34.22 \pm 5.34$  kJ/mol using the thermochemical cycles listed in Table S1.

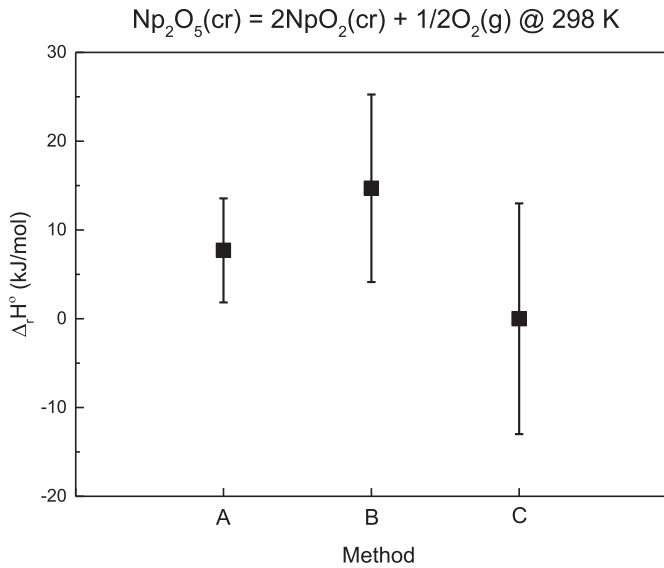
The drop solution enthalpies  $\Delta H_{\text{DS}}$  measured here include  $\Delta H_{\text{HC}}$  and  $\Delta H_{\text{S}}$ , where  $\Delta H_{\text{HC}}$  is the heat content of oxide from 298 to 973 K, and  $\Delta H_{\text{S}}$  is the heat of solution in the molten solvent at 973 K.  $\Delta H_{\text{HC}}$  can be calculated from the heat capacity ( $C_p$ ) data [35] and is shown in Table 2. With the measured  $\Delta H_{\text{DS}}$  listed in Table 2, we calculated  $\Delta H_{\text{S}}$  of the neptunium oxides along with those of uranium oxides and thorium oxide. For comparison, the results are given per mole of actinide metal.  $\Delta H_{\text{S}}(\text{NpO}_{2.5})$  is comparable to  $\Delta H_{\text{S}}(\gamma\text{-UO}_3)$  and  $\Delta H_{\text{S}}(\text{ThO}_2)$ , where  $\Delta H_{\text{S}}$  of these oxides result from the heat of solution without oxidation. However,  $\Delta H_{\text{HC}}(\text{NpO}_{2.5})$  was estimated by high temperature heat capacity measured by drop calorimetry from 350 to 750 K by Belyaev et al. [20], which gives  $C_p(\text{T})/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 99.2 + 98.6 \times 10^{-3} (\text{T/K})$ , since  $\text{Np}_2\text{O}_5$  is unstable at high temperature.  $\Delta H_{\text{HC}}(\text{NpO}_{2.5})$  may be underestimated to be consistent with the variation of  $\Delta H_{\text{HC}}$  of uranium oxides, so  $\Delta H_{\text{S}}(\text{NpO}_{2.5})$  is likely more negative, and closer to the values of  $\Delta H_{\text{S}}(\gamma\text{-UO}_3)$  and  $\Delta H_{\text{S}}(\text{ThO}_2)$ .

The enthalpy of decomposition of  $\text{Np}_2\text{O}_5$  to  $\text{NpO}_2$  and  $\text{O}_2$  at 298 K, representing the reaction



Is calculated by the thermochemical cycles listed in Table S2 and is  $7.70 \pm 5.86$  kJ/mol, obtained directly from the measurements of drop solution enthalpies of these two neptunium oxides.

The enthalpy of formation of  $\text{NpO}_2$  from the elements was previously measured by Huber and Holley [19] by oxygen bomb calorimetry using 1.5–2 g of neptunium metal pellets in each experiment, giving  $\Delta_f H^\circ_{298}(\text{NpO}_2) = -1074.2 \pm 2.5$  kJ/mol [19]. The enthalpy of formation of  $\text{Np}_2\text{O}_5$  from the elements has been measured by solution calorimetry by two slightly different methods. Merli and Fuger [18] reported  $\Delta_f H^\circ_{298}(\text{Np}_2\text{O}_5) = -2162.7 \pm 9.3$  kJ/mol using 2–12 mg of material, and Belyaev [17] reported  $\Delta_f H^\circ_{298}(\text{Np}_2\text{O}_5) = -2148 \pm 12$  kJ/mol using 37–73 mg of material. The decomposition enthalpy of  $\text{Np}_2\text{O}_5$  is also calculated from these reported data and compared with that from this work (Fig. 1 and Table 3). Our new value ( $7.70 \pm 5.86$  kJ/mol) is in reasonable agreement with both values ( $14.3 \pm 10.6$  kJ/mol and  $-0.4 \pm 13.0$  kJ/mol), and yields a smaller error while using only 5 mg of sample via direct solution calorimetric measurements.



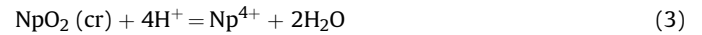
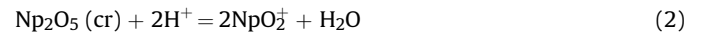
**Fig. 1.** Enthalpy of decomposition for the reaction  $\text{Np}_2\text{O}_5 \rightarrow 2\text{NpO}_2 + 1/2\text{O}_2$  at 298 K measured by high temperature drop solution calorimetry (this work), compared with values measured by oxygen bomb calorimetry and solution calorimetry. Method A: direct measurement in this work; Method B: calculated from  $\Delta_f H^\circ(\text{NpO}_2)$  [19] and  $\Delta_f H^\circ(\text{Np}_2\text{O}_5)$  [18]; Method C: calculated from  $\Delta_f H^\circ(\text{NpO}_2)$  [19] and  $\Delta_f H^\circ(\text{Np}_2\text{O}_5)$  [17].

The entropy of reaction (1) can be calculated using standard entropies given in Table 3.  $S^\circ_{298}(\text{NpO}_2) = 80.29 \pm 0.42 \text{ J K}^{-1} \text{ mol}^{-1}$  based on its measured low temperature heat capacity [21]. The low temperature heat capacity of  $\text{Np}_2\text{O}_5$  has not been measured, and Merli and Fuger [18] have estimated  $S^\circ_{298}(\text{Np}_2\text{O}_5) = 186 \pm 16 \text{ J K}^{-1} \text{ mol}^{-1}$ , which is consistent with the variation of the standard entropy of uranium oxides based on the difference in oxygen stoichiometry [35]. Using these values and the well-known standard entropy of oxygen gas (Table 3), one gets

$\Delta S^\circ = 77.10 \pm 16 \text{ J K}^{-1} \text{ mol}^{-1}$ , the large error reflecting the uncertainty in estimating the entropy of  $\text{Np}_2\text{O}_5$ . This large positive entropy change results from the production of oxygen gas. Neglecting heat capacity differences, one can then write the Gibbs free energy change for reaction (1) as  $\Delta G = \Delta H - T\Delta S = 7700 - 77.10T \text{ J mol}^{-1}$ . The decomposition temperature in a pure oxygen atmosphere is then calculated to be  $T_{\text{decomp}} = 7700/77.10 = 100 \text{ K}$ . The highest decomposition temperature consistent with the uncertainties in the above data can be obtained by taking the most endothermic enthalpy of decomposition and the smallest entropy of decomposition, so  $T_{\text{decomp, max}} = 13,560/61.10 = 222 \text{ K}$ . The thermodynamic calculations strongly suggest that,  $\text{NpO}_2$  may be the thermodynamically stable neptunium solid oxide phase for the long term, since the calculations show an equilibrium decomposition temperature below 298 K. This is consistent with a recent study which has shown that  $\text{NpO}_2$  can precipitate from neptunyl solutions under mildly oxidizing conditions [7,8]. It is also consistent with the observation that  $\text{Np}_2\text{O}_5$  decomposition appears to be irreversible, and that  $\text{Np}_2\text{O}_5$  has never been reported to be synthesized by the direct oxidation of  $\text{NpO}_2$ ; on the other hand,  $\text{Np}_2\text{O}_5$  is always synthesized hydrothermally from aqueous solution of neptunyl species, consistent with  $\text{Np(V)}$  oxide being metastable.

The present data allow the calculation of free energies of formation of the neptunium oxides from the elements ( $\Delta_f G^\circ_{298}$ ), giving values of  $-1022.0 \pm 2.5 \text{ kJ mol}^{-1}$  for  $\text{NpO}_2$  and  $-2028.3 \pm 13.6 \text{ kJ mol}^{-1}$  for  $\text{Np}_2\text{O}_5$ , using the enthalpy and entropy values in Table 3.

We can also calculate  $\Delta_f G^\circ_{298}$  from solubility experiments by  $\Delta G^\circ = -2.303RT \log K^\circ$  for the following reactions involving neptunium oxides,



Where the  $\Delta_f G^\circ_{298}(\text{NpO}_2^+)$  and  $\Delta_f G^\circ_{298}(\text{Np}^{4+})$  are calculated from

**Table 3**

Thermodynamic data at 298 K for neptunium oxides from thermochemical measurements and estimation of decomposition temperature of  $\text{Np}_2\text{O}_5$ .

Thermodynamic data	Selected or calculated values		
$\Delta_f H^\circ_{298}(\text{NpO}_2)$ (kJ/mol)	$-1074.2 \pm 2.5$ [19]		
$\Delta_f H^\circ_{298}(\text{Np}_2\text{O}_5)$ (kJ/mol)	$-2162.7 \pm 9.3$ [18]	$-2148 \pm 12$ [17]	—
$\Delta_{\text{rxn}} H^\circ(\text{Np}_2\text{O}_5 = 2\text{NpO}_2 + 1/2\text{O}_2)$ (kJ/mol)	$14.3 \pm 10.6$	$-0.4 \pm 13.0$	$7.70 \pm 5.86^a$
$S^\circ_{298}(\text{Np})$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$50.45 \pm 0.4$ [44]		
$S^\circ_{298}(\text{NpO}_2)$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$80.29 \pm 0.42$ [21]		
$S^\circ_{298}(\text{Np}_2\text{O}_5)$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$186 \pm 15$ [35]		
$S^\circ_{298}(\text{O}_2)$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$205.043$ [41]		
$\Delta_f G^\circ_{298}(\text{NpO}_2)$ (kJ/mol)	$-1022.0 \pm 2.5$		
$\Delta_f G^\circ_{298}(\text{Np}_2\text{O}_5)$ (kJ/mol)	$-2035.3 \pm 14.5$	$-2020.6 \pm 16.4$	$-2028.3 \pm 13.6$
Decomposition temperature (K)	$185 \pm 142$	0 to 168	$100 \pm 78$

<sup>a</sup> This work.

**Table 4**

Thermodynamic data at 298 K for neptunium oxides calculated from solubility experiments.

Thermodynamic data	Selected or calculated values		
$\Delta_f G^\circ_{298}(\text{NpO}_2^+)$ (kJ/mol)	$-795.8 \pm 5.4$ [45]		
$E^\circ(\text{NpO}_2^+/\text{NpO}_2)$ (V)	$1.161 \pm 0.014$ [37]	$1.193 \pm 0.043$ [38]	$0.96$ [39]
$E^\circ(\text{NpO}_2^+/\text{Np}^{4+})$ (V)	$0.596 \pm 0.078$ [37]	$0.660 \pm 0.067$ [38]	$0.07$ [39]
$\Delta_f G^\circ_{298}(\text{NpO}_2)$ (kJ/mol)	$-907.9 \pm 5.8$ [37]	$-910.9 \pm 6.8$	$-888.4 \pm 5.4$
$\Delta_f G^\circ_{298}(\text{Np}^{4+})$ (kJ/mol)	$-491.1 \pm 9.5$ [37]	$-500.2 \pm 9.4$	$-420.8 \pm 5.4$
$\log K_1^\circ$	$5.2 \pm 0.8$ [46]		
$\log K_2^\circ$	$-9.9 \pm 1.7$ [37]		
$\Delta_f G^\circ_{298}(\text{NpO}_2)$ (kJ/mol)	$-1021.8 \pm 13.5$ [37]	$-1031.0 \pm 13.5$	$-951.6 \pm 11.1$
$\Delta_f G^\circ_{298}(\text{Np}_2\text{O}_5)$ (kJ/mol)	$-2023.3 \pm 12.4$ [37]	$-2029.4 \pm 14.4$	$-1984.4 \pm 11.7$
Reference	Kaszuba et al. [37].	Kihara et al. [38].	Chatterjee et al. [39].



the  $\Delta_f G^\circ_{298}(\text{NpO}_2^{2+})$  [36], and the standard potential for the  $\text{NpO}_2^{2+}/\text{NpO}_2$  and  $\text{NpO}_2^{2+}/\text{Np}^{4+}$  couples by  $\Delta G^\circ = nFE^\circ$ . Table 4 lists the  $\Delta_f G^\circ_{298}(\text{NpO}_2)$  and  $\Delta_f G^\circ_{298}(\text{Np}_2\text{O}_5)$  calculated by Kaszuba et al. [37]. Using the  $E^\circ(\text{NpO}_2^{2+}/\text{NpO}_2)$  and  $E^\circ(\text{NpO}_2^{2+}/\text{Np}^{4+})$  summarized by Kihara et al. [38], we also calculate the  $\Delta_f G^\circ_{298}(\text{NpO}_2)$  and  $\Delta_f G^\circ_{298}(\text{Np}_2\text{O}_5)$  (Table 4). Comparing the data for the standard formation Gibbs energy of both neptunium oxides, the data measured by solubility experiments (Table 4) agree within experimental error with the ones obtained by direct thermochemical measurements (Table 3). On the other hand, using a recent work [39] reporting standard potentials for neptunium redox reactions, which are claimed to have higher accuracy, the calculated  $\Delta_f G^\circ$  values are much less negative (Table 4), and not consistent with any other reported values. Our results show that the direct calorimetric measurements are consistent with the existing thermodynamic database.

There is inconsistency in the Facility for the Analysis of Chemical Thermodynamics (F\*A\*C\*T) database concerning the thermodynamic properties of neptunium oxides. The critically evaluated F\*A\*C\*T database gives less negative values of  $\Delta_f H^\circ_{298}(\text{NpO}_2) = -1029.264$  kJ/mol and  $\Delta_f G^\circ_{298}(\text{NpO}_2) = -974.619$  kJ/mol [40]. There are no such data for  $\text{Np}_2\text{O}_5$ . Fahey et al. [34] measured the oxygen pressure – temperature dependence for decomposition of  $\text{Np}_2\text{O}_5(\text{cr}) \rightarrow 2\text{NpO}_2(\text{cr}) + 1/2\text{O}_2(\text{g})$ , yielding  $\log[P_{\text{O}_2}(\text{atm})] = 11.95 - 10,520/T$  and  $RT\ln[P_{\text{O}_2}(\text{atm})] = -201,400 + 229T$  (J/mol). Using  $\Delta G^\circ_T = -1/2 RT\ln[P_{\text{O}_2}(\text{atm})] = \Delta H^\circ_{298} - T\Delta S^\circ_{298} = 100,700 - 114.5T$  (J/mol), one gets  $\Delta H^\circ_{298} = 100.7$  kJ/mol and  $\Delta S^\circ_{298} = 114.5 \text{ J K}^{-1} \text{ mol}^{-1}$ , hence  $S^\circ_{298}(\text{Np}_2\text{O}_5) = 148.6 \text{ J K}^{-1} \text{ mol}^{-1}$ . This enthalpy change value may be close to that of reduction of  $\text{UO}_3$  to  $\text{UO}_2$ , which is  $138.9 \pm 1.3$  kJ/mol [41];  $S^\circ_{298}(\text{Np}_2\text{O}_5)$ , however, is unreasonably low for a higher actinide oxide since  $S^\circ_{298}(\text{NpO}_2) = 80.29 \pm 0.42 \text{ J K}^{-1} \text{ mol}^{-1}$  [21]. It also indicates the decomposition temperature of  $\text{Np}_2\text{O}_5$  at 1 atm oxygen is 880 K, much higher than our new data suggest.

Smith et al. [36] optimized formation enthalpies  $\Delta_f H^\circ_{298}(\text{NpO}_2) = -1076.8$  kJ/mol and  $\Delta_f H^\circ_{298}(\text{Np}_2\text{O}_5) = -2172.0$  kJ/mol by thermodynamic modeling using the CALPHAD methodology. Their calculated enthalpy and entropy values for  $\text{NpO}_2$  are in good agreement with reported data (Table 3). However, their optimized  $\Delta_f H^\circ_{298}(\text{Np}_2\text{O}_5) = -2172.0$  kJ/mol is more negative than the two reported values ( $-2162.7 \pm 9.3$  kJ/mol and  $-2148 \pm 12$  kJ/mol). They also reported optimized entropies  $S^\circ_{298}(\text{NpO}_2) = 80.3 \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $S^\circ_{298}(\text{Np}_2\text{O}_5) = 242.2 \text{ J K}^{-1} \text{ mol}^{-1}$  (as the low-temperature heat capacity of  $\text{Np}_2\text{O}_5$  has not been measured). Hence we can calculate  $\Delta_f G^\circ_{298}(\text{NpO}_2) = -1024.6$  kJ/mol, which agrees with the experimental data; and  $\Delta_f G^\circ_{298}(\text{Np}_2\text{O}_5) = -2061.4$  kJ/mol, which is significantly more negative than the other data (Table 3). This substantial discrepancy in Gibbs free energy of  $\text{Np}_2\text{O}_5$  is the result of the authors using a larger  $S^\circ_{298}(\text{Np}_2\text{O}_5)$  to accommodate their assumed higher decomposition temperature (888 K) of  $\text{Np}_2\text{O}_5$ . This assumption cannot justify their optimization of thermochemical data. As discussed above, we conclude that  $\text{NpO}_2$  is the thermodynamically stable oxide while  $\text{Np}_2\text{O}_5$  is metastable. Even as shown in many previous works [15,33,34] and confirmed in this study,  $\text{Np}_2\text{O}_5$  can persist up to 973 K, the various reported decomposition temperatures do not represent equilibrium. Clearly it would be highly desirable to measure the low temperature heat capacity and calculate the standard entropy of  $\text{Np}_2\text{O}_5$ , which can be done on much smaller samples using modern relaxation calorimetric techniques (calorimeter on a chip) [42].

We have demonstrated in this paper that high temperature oxide melt solution calorimetry of neptunium oxides is straightforward and produces reliable data, while requiring only milligram quantities of material. Calorimetric studies of heats of formation of neptunium compounds are ongoing for carefully characterized synthetic materials, such as analogs to uranyl minerals and

nanoscale clusters. These thermodynamic data will establish the stability of neptunium materials, and increase understanding of processes that occur during the dissolution of spent nuclear fuel and the transport of actinides in an aqueous environment.

## 5. Conclusion

Neptunium oxides ( $\text{Np}_2\text{O}_5$  and  $\text{NpO}_2$ ) have been synthesized and characterized, and their thermochemical properties have been studied by high temperature oxide melt solution calorimetry for the first time. Neptunium compounds readily dissolve in molten sodium molybdate solvent at 973 K. After dissolution, neptunium is stable in the pentavalent state under oxidizing conditions in the calorimeter. The drop solution enthalpies of  $\text{Np}_2\text{O}_5$  and  $\text{NpO}_2$  have been measured using milligram-scale samples and the enthalpy of the decomposition reaction,  $\text{Np}_2\text{O}_5(\text{cr}) = 2\text{NpO}_2(\text{cr}) + 1/2\text{O}_2(\text{g})$  at 298 K, is determined to be  $7.70 \pm 5.86$  kJ/mol. This direct measurement is in agreement with existing thermodynamic data, showing that  $\text{NpO}_2$  is the thermodynamically stable oxide over the long term, while  $\text{Np}_2\text{O}_5$  is metastable and may persist up to 973 K.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jnucmat.2017.10.034>.

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